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Meteorology. — *"The treatment of wind-observations."* By Dr. J. P. VAN DER STOK.

(Communicated in the meeting of February 23, 1907).

1. When working out wind-observations we directly meet with the difficulty that a method holding generally, in which the characteristics of a wind distribution come to the fore in condensed form, does not exist. The discussion held for many a year concerning the desirability or not of an application of LAMBERT's formula, i. e. of the calculation of the vectorial mean of velocity or force has not led to a definite result and the consequence is that for regions where trade- and monsoon winds prevail the calculation of this mean can be applied, not for higher latitudes, so that here we have to judge by extensive tables of frequencies of direction and mean velocities, independent of direction.

When working out the wind-observations made at Batavia I did not hesitate to make an extensive use of this formula; the same method has been followed in the atlas for the East Indian Archipelago; but in order to give at least a notion of the value of the velocities annulling each other here I have added to the resulting movement (called by HANN *windpath*) a so-called factor of stability. If namely the wind were perfectly stable, the vectorial mean would be equal to the mean independent of the direction and the stability would amount to 100 %, which percentage becomes smaller and smaller according to the direction of the wind becoming more variable. So here attention is drawn to the fact, that a part of the observations is eliminated, but it is not indicated what character this vanishing part has which becomes chief in our regions.

In the climatological atlas lately published of British India the same method is followed; in the "Klima Tabeller for Norge" MOHN gives but the above mentioned tables without calculation of the vectorial mean, which is, indeed, of slight importance for this climate.

The same uncertainty is found in the graphical representation of a wind distribution by so-called windroses; almost everyone who has been occupied in arranging books of prints has projected windroses of his own; some of those roses, as e. g. in the "Vierteljahrskarte für die Nordsee und Ostsee" published by the "Deutsche Seewarte", show only the frequencies of direction without velocities; in others, as e. g. those shown in the above atlas of the East Indies, each direction is taken into account with the velocity belonging to it as weight, so that mean velocities are represented. All these roses

furnish discontinuous quantities and change their aspect according to their boundaries being taken differently.

In BUCHAN's general meteorological atlas no roses are projected, only arrows indicating the most frequent direction without heeding the force, and in the "Segelhandbuch für den Atlantischen Ozean" published by the "Deutsche Seewarte" for higher latitudes where the wind is variable the use of wind-observations is entirely done away with and arrows have been drawn in accordance with the course of the mean isobars on account of the law of BUYS BALLOT, where a constant angle of 68° between gradient and direction of wind has been assumed.

This short survey of the manner in which in the most recent standard works this problem has been treated may show that indeed there is as yet no question about a satisfactory solution, as has already been observed.

The aim of this communication is to hit upon a general method of operation and representation of an arbitrary wind distribution in which to the variable part also justice is done, whilst the graphical representation has a continuous course and shows at a glance the five characteristic quantities which mark each wind distribution and which may be, therefore, called the *wind-constants*.

The method proposed here is founded on the basis of the calculus of probability, but it is important to notice that it is not at all bound to it; at the bottom it is the same which is generally applied in the treatment of directed quantities: distribution of masses and forces in mechanics, the theory of elasticity, the law of radiation and the theory of errors in a plane.

2. A wind-observation can be represented by a point in a plane such that the distance to an assumed origin is a measure for the velocity of the wind (or force) and that the angle made by the radius vector with the Y (North) axis counted from N. to E. indicates the direction. If in this way all observations, N in number, are drawn and if we think that to each point an equal mass is connected, then in general the centre of gravity will not coincide with the origin selected; its situation may be determined by the quantities R_0 and α. The distribution of the masses around the centre of gravity, is then characterized by the lengths M and M' of the two principal axes of inertia and the angle β enclosed by the axes M and Y.

As is known the five constants by which such a system is characterized can be calculated according to this purely mechanic notion by determining the moments M_x and M_y with respect to the axes

and the moments of inertia M_x^2 and M_y^2 and M_{xy}, which furnish the five equations necessary for the calculation of the unknown quantities.

We arrive at quite the same equations when the distribution of the winds according to direction and velocity is regarded as a system of accidental, directed quantities in a plane. The centre of gravity then represents according to size and direction the constant part of the wind which is supposed to be connected with all observations and of which, therefore, the probability is equal to unity; the axes of inertia become principal axes of probability and the lengths M and M' are replaced by the reciprocal lengths h and h', so that

$$h^2 = \frac{1}{2M^2} \quad , \quad h'^2 = \frac{1}{2M'^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The sum of the masses is put equal to unity and for the probability that an observation lies between the limits R and $R + dR$ of velocity and θ and $\theta + d\theta$ as far as direction is concerned the expression holds

$$\frac{hh'}{\pi} e^{-f(R,\theta)} R\, dR\, d\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where:

$$f(R,\theta) = h^2 [R\cos(\theta-\beta) - R_0 \cos(\alpha-\beta)]^2 + h'^2 [R\sin(\theta-\beta) - R_0 \sin(\alpha-\beta)]^2 . \quad (3)$$

In the language of the theory of errors (R_0, α) would be the so-called constant error, M and M' the greatest and smallest projections of the mean errors. As observations of wind agree still less than other meteorological quantities with the opinion held in the theory of errors, where the constant part is regarded as the end of the operation and the variable quantities as deviations, it is desirable when applying the calculus of probability to quantities of this kind to be entirely free of the terminology used in the theory of errors, but which would be here without meaning and which would give rise to misunderstanding.

The treatment must also differ somewhat from that of erroneous quantities, it being if not impossible at least impractical to correct all the observations for the constant part.

3. As examples of treatment two series of observations have been selected from the treated material.

a. Observations of wind performed at Bergen (Norway) during 20 years, 1885—1904, three times daily at 8 A.M, 2 P.M. and 8 P.M. The velocity (or force) of the wind is expressed in the so-called

half scale of BEAUFORT (1—6) (Jahrbuch des Norwegischen Meteorol. Instituts, Christiania).

b. Observations of wind performed at Falmouth (Channel) during 17 years, 1874—1886 and 1900—1903; the observations made in the years 1887—1899 are published in such a way as to be useless for this investigation.

Observations have been used, made daily six times: at noon, 4 P.M., 8 P.M., midnight, 4 A.M. and 8 A.M.; the velocity of wind is expressed in English (statute) miles an hour (Hourly readings obtained from the selfrecording instruments etc. London).

With respect to the force of the wind estimated at Bergen is to be noticed that in this communication these scale-values are regarded not as forces but as velocities, although in reality they are neither one nor the other. According to a recent extensive investigation [1]) the ratio of the Beaufort values to corresponding velocities can be indicated by the following numbers

BEAUFORT	velocity meters a second	ratio	BEAUFORT	velocity meters a second	ratio
0	1.34	—	6	10.95	1.83
1	2.24	2.24	7	13.41	1.92
2	3.58	1.79	8	16.09	2.01
3	4.92	1.64	9	19.67	2.19
4	6.71	1.68	10	23.69	2.34
5	8.72	1.74			

As the various velocities do not appear in an equal number the total mean out of these ratios would not give a fit factor of reduction for mean BEAUFORT-values; so a certain weight must be assigned to each separate ratio. For this the frequencies have been used of the 36000 wind-velocities observed at Falmouth calculated for a whole year; in this way has been found for the reduction-factor 1.83; the English measure, miles an hour, can be reduced to m. a. s. and BEAUFORT scale-values by means of multiplication respectively by

0.447 and 0.244.

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[1]) The BEAUFORT scale of windforce.
Report of the Director of the Meteor. Office upon an Inquiry into the Relation between the Estimates of Windforce according to Admiral BEAUFORT's Scale and the velocities recorded by Anemometers. London, 1906.

4. The calculation of the five charateristic constants of a wind distribution amounts in one respect to the integration of (2), in another respect to the means applied in this integration to a given set of observations.

The integration of (2) takes place by the introduction of rectangular coordinates :

$$x = R \sin \theta \quad , \quad y = R \cos \theta,$$

where the element $RdRd\theta$ is replaced by the element $dxdy$, whilst the limits which were ∞ and 0 for R, 2π and 0 for θ, now become ∞ and $-\infty$.

Then the expression (2) under the sign of the integral is multiplied successively by

$$x,\ y,\ x^2,\ y^2 \text{ and } xy.$$

If we then put :

$$R_0 \cos(\alpha-\beta) = a, \qquad x = x' \sin\beta + y' \cos\beta,$$

$$R_0 \sin(\alpha-\beta) = b, \qquad y = x' \cos\beta - y' \sin\beta,$$

the variables x' and y' can be separated and the integration can be done; in this way we find for the determination of the five quantities to be obtained the five equations :

$$\left.\begin{aligned} M_x &= a\cos\beta - b\sin\beta, \quad M_y = a\sin\beta + b\cos\beta \\ M_x^2 &= \frac{\cos^2\beta}{2h^2} + \frac{\sin^2\beta}{2h'^2} + a^2\cos^2\beta + b^2\sin^2\beta - ab\sin 2\beta \\ M_y^2 &= \frac{\sin^2\beta}{2h^2} + \frac{\cos^2\beta}{2h'^2} + a^2\sin^2\beta + b^2\cos^2\beta + ab\sin 2\beta \\ 2M_{xy} &= \left(\frac{1}{2h^2} - \frac{1}{2h'^2}\right)\sin 2\beta + (a^2 - b^2)\sin 2\beta + ab\cos 2\beta \end{aligned}\right\}, \quad (3)$$

out of which, on account of (1)

$$\left.\begin{aligned} M_x &= R_0\cos\alpha, \quad M_y = R_0\sin\alpha \\ M_x^2 + M_y^2 - [(M_x)^2 + (M_y)^2] &= M^2 + M'^2 \\ M_x^2 - M_y^2 - [(M_x)^2 - (M_y)^2] &= (M^2 - M'^2)\cos 2\beta \\ 2M_{xy} - 2M_xM_y &= (M^2 - M'^2)\sin 2\beta \end{aligned}\right\} \quad . \quad . \quad (4)$$

TABLE I. Frequencies of the wind.

Bergen. June.

In half BEAUFORT scale-values.

	0	1	2	3	4	5	Sum
C	261	—	—	—	—	—	261
N		59	30	29	5	2	125
NNE		6	6	1	—	—	13
NE		6	2	—	—	—	8
ENE		3	2	—	—	—	5
E		13	—	—	—	—	13
ESE		4	1	—	—	—	5
SE		24	3	1	—	—	28
SSE		40	16	3	—	—	59
S		115	54	22	6	—	197
SSW		56	39	15	4	—	114
SW		25	10	2	2	—	39
WSW		9	2	—	—	—	11
W		98	26	5	—	—	129
WNW		99	24	1	—	—	124
NW		190	51	6	—	—	247
NNW		246	118	46	12	—	422
Sum	261	993	384	131	29	2	1800

5. In order to apply the formulae (4) to a given set of observations we must compose for each period, e.g. each month, in the first place a table of frequency of direction and velocity, which can be easily done. In Table I such a composition has been given as an example.

Further out of this table have been calculated the products of these frequencies f with the scale-values R, the latter counted double, so that the products have been expressed in the ordinary BEAUFORT scale; finally these products have been once again multiplied by the corresponding scale-values (fR^2); in this simple way we find the sums.

TABLE II.

	fR	fR^2		fR	fR^2
N	472	2280	S	626	1500
NNE	42	156	SSW	390	1644
NE	20	56	SW	118	460
ENE	14	44	WSW	26	68
E	26	52	W	330	988
ESE	12	32	WNW	300	816
SE	66	180	NW	620	1792
SSE	162	524	NNW	1336	5296
			Som	4560	16888

The sums fR, multiplied respectively by $\cos\theta$ and $\sin\theta$ and divided by 1800, immediately furnish the quantities M_x and M_y; the sums fR^2 must be multiplied successively by $\cos^2\theta$, $\sin^2\theta$ and $\sin\theta\cos\theta$.

It is easier to multiply the latter sums by $\cos 2\theta$ and $\sin 2\theta$; if the total mean is S, we find:

$$M_x^2 = fR^2\cos^2\theta = \tfrac{1}{2}S + \tfrac{1}{2}fR^2\cos 2\theta$$
$$M_y^2 = fR^2\sin^2\theta = \tfrac{1}{2}S - \tfrac{1}{2}fR^2\cos 2\theta$$
$$2M_{xy} = fR^2\sin 2\theta.$$

So the whole operation greatly resembles the calculation of FOURIER terms; indeed, also by the way of operation indicated here an analysis of the movement of the air is obtained.

In the Tables III and IV we find the values of the wind-constants calculated in this way; besides the five characteristic quantities we find still given as quantities practically serviceable for various ends:

$e = \dfrac{\sqrt{M^2 - M'^2}}{M}$, the excentricity of the ellipse of which M and M' represent the half principal axes,

(R_0' and α') the resultants of the squares of the velocities giving an image of the mean flux of energy,

$\bar{V}$ the mean velocity independent of the direction,

$\bar{V}^2$ the mean square of the velocity independent of the direction, i. e. a measure for the total energy; this quantity is according to (4) analogous to the square of the mean error, not corrected for the constant part, in the theory of errors,

N the number of used observations.

TABLE IIIa Constants of the wind.
Bergen 1885—1904.
In BEAUFORT scale-values.

	R_o	α	M	M'	β	e
January	1.84	179°	3.39	1.65	174°	0.873
February	1.51	180	3.10	1.59	172	0.858
March	1.16	183	3.25	1.60	171	0.872
April	0.40	2 5	2.88	1.47	169	0.859
May	0.68	284	2.84	1.37	169	0.879
June	1.07	302	2.61	1.19	171	0.891
July	0.93	276	2.64	1.22	168	0.885
August	0.73	251	2.86	1.22	168	0.904
September	0 97	212	2 88	1.38	174	0.876
October	1.10	182	2.94	1.52	171	0.857
November	1.51	179	3 10	1.48	171	0.880
December	1.78	179	3 14	1 57	174	0 866
Year	0.85	203	2.97	1.44	171	0.875

TABLE IIIb Constants of the wind.
Bergen 1885—1904.
In BEAUFORT scale-values.

	R'_o	α'	$\overline{V}$	$\overline{V^2}$	N
January	10.56	182°	3.31	17.63	1860
February	8.09	184	2.90	14.44	1695
March	5.96	186	3.06	14.48	1860
April	1.62	224	2.64	10.61	1800
May	2.62	281	2.59	10.39	1860
June	3.78	305	2.53	9.38	1800
July	3.19	272	2 58	9.32	1860
August	2.79	243	2.63	10.18	1860
September	4.30	215	2.67	11.14	1800
October	5.13	185	2.76	12.19	1860
November	7.77	182	2.91	14.09	1800
December	9.30	183	3.06	15.50	1860
Year	4.42	200	2.80	12.45	21915

TABLE IVa. Constants of the wind.
Falmouth. 1874—1886, 1900—1903.
In Eng. miles an hour.

	R_o	α	M	M'	β	e
January	5.23	211°	15.20	13.93	73°	0.400
February	5.33	209	14.08	13.25	164	0.339
March	3.56	255	15.02	13.26	67	0.470
April	0.85	215	13.70	12.21	72	0.454
May	2.34	255	12 02	11.52	40	0.286
June	4.60	255	11.19	10.07	158	0.436
July	6.46	254	10.39	8.92	155	0.507
August	5.79	245	10.48	9.76	82	0.363
September	3.77	229	11.05	10.67	164	0.260
October	3.56	239	13.51	13.03	81	0.266
November	4.57	248	13.75	13.03	93	0.318
December	5.69	243	13.69	12.98	22	0.318
Year	4.14	239	12.60	12.43	96	0.166

TABLE IVb. Constants of the wind.
Falmouth.

	R'_o	α'	$\overline{V}$	$\overline{V^2}$	N
January	146.0	205°	18.4	452.5	2821
February	159.9	203	16.9	402.1	2675
March	88.8	241	17.5	414.2	2930
April	23.0	178	15.7	337.4	2879
May	54.1	241	14.4	282.5	3140
June	92.4	252	13.7	247.8	3015
July	122.2	252	12.9	228.5	3060
August	122.0	242	13.0	238.7	3154
September	83.7	224	13.1	250.3	3047
October	78.5	223	16.4	370.0	3154
November	114.2	237	16.6	379.7	3053
December	148.6	233	16.6	388.4	2888
Year	98.2	229	15.4	330.4	35816

A closer discussion of the results arrived at in this way may for shortness' sake be left out; however, the observation is not superfluous that the two examples represent two types, a reason why they were chosen. At Bergen the ellipse of the variable winds is very constant of shape and the excentricity is very great; at Falmouth the difference between M and M' is always very slight and the differences found there are evidently to be regarded rather as accidental arithmetical results than as facts, the angle β being subject to great and irregular oscillations; evidently the ellipse approaches a circle, so that in form (2) we may put $h = h'$. This leading to a considerable simplification of the formula, these observations at Falmouth are eminently fit for comparison of the results of calculation and observation, whilst also the fact that here real velocities have been observed with well-verified instruments, makes this series very favourable.

6. The expression (2) shows: the probability that an observation lies between the limits R and $R + dR$, θ and $\theta + d\theta$; the same expression without the element $RdRd\theta$ indicates: the specific probability of a wind (R,θ) i.e. the probability with respect to the unity of surface when one imagines this surface to be small. If we put for simplification:

$$h'^2 + h^2 = 2p, \quad h'^2 - h^2 = 2q, \quad R_0^2 (p - q \cos 2(\alpha - \beta)) = \mu$$

$$(p - q \cos 2(\theta - \beta)) = \nu, \quad s^2 = R_0^2 (p^2 + q^2 - 2pq \cos 2(\alpha - \beta))$$

$$s \cos (\theta - \varphi) = \lambda \quad \operatorname{tang} \varphi = \frac{p \sin \alpha + q \sin (\alpha - 2\beta)}{p \cos \alpha - q \cos (\alpha - 2\beta)},$$

then (2) takes the form:

$$\frac{\sqrt{p^2 - q^2}}{\pi} e^{-R^2\nu + 2R\lambda - \mu} RdRd\theta. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If here we put:

$$R^2\nu - 2R\lambda + \mu = c \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

then it follows out of the above formulated definition that the specific probability of all observations lying on the circumference of the excentric ellipse (6) is the same and equal to:

$$\frac{\sqrt{p^2 - q^2}}{\pi} e^{-c}.$$

The probability that the velocity of the wind does not surpass the value R_c expressed by (6) in function of θ, in other words the number of observations which are to lie within the area of the ellipse, is

found by integrating (5), first with respect to R between the limits R_c and 0, then with respect to θ between 2π and 0.

For the simple case $R_0 = 0$, so also $\mu = 0$ and $\lambda = 0$, the first integration gives immediately

$$\frac{\sqrt{p^2-q^2}}{\pi} \cdot \frac{1-e^{-c}}{2v}$$

and as

$$\frac{\sqrt{p^2-q^2}}{2\pi} \int_0^{2\pi} \frac{d\theta}{v} = 1,$$

the probability to be found becomes simply:

$$1-e^{-c} \quad \ldots \ldots \ldots \ldots \ldots \quad (7)$$

and the number of observations lying inside the circumference of the ellipse (6):

$$N(1-e^{-c}).$$

This amount remaining the same whether we regard the ellipse (6) from the excentric origin or from the centre, i.e. for $R_0 = 0$, if with the integration the limits are changed correspondingly, the expression (7) must also be accurate when R_0 is not equal to zero and must thus hold in general.

Indeed, an other simplification, namely $q = 0$ (which is applicable to the results for Falmouth) leads to a set of definite integrals, which can be evaluated and which confirm this conclusion.

Amongst the series of ellipses represented by (6) two are remarkable; if we assign to c the value 0.5, then on account of (1) the half axes of the ellipse become equal to the greatest and smallest projections M and M' of the mean velocities, so that the ellipse (6) then represents what we might call the *specific* or *typical windellipse*, thus a kind of windrose, in which the characteristic qualities of the wind-distribution under consideration immediately become conspicuous.

The radius vector R_m drawn to an arbitrary point in the circumference is given in the direction determined by that choice by the equation:

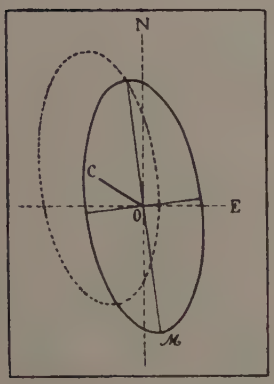
$$2R^2_m v - 4R_m \lambda + 2\mu - 1 = 0.$$

The probability that a velocity does not surpass this value is:

$$1 - e^{-1/2} = 0.39347.$$

So among a thousand observations there will be 393 lying inside this typical ellipse whilst the specific probability of each of the velocities R_m is:

$$0.6065 \frac{\sqrt{p^2-q^2}}{\pi}.$$



In the given diagram such a typical windellipse is represented for Bergen in the month of June by the dotted line; the vector OC represents here the constant part (R_0, α), the half axes are equal to M and M', and the angle $NOM = \beta$; one millimeter corresponds to $^2/_{10}$ BEAUFORT scale-value or to $^2/_{10} \times 1.83 = 0.275$ meter a second.

If necessary this diagram might be amplified with two circles, one of a radius

$$\sqrt{M^2 + M'^2},$$

representing the mean monthly wind velocity corrected for the constant part, the other described with radius

$$\sqrt{M^2 + M'^2 + (M_x)^2 + (M_y)^2},$$

which is according to (4) a measure for the mean total velocity, corresponding to the square root of the quantity V^2 of the tables III and IV.

An other remarkable ellipse which might be called the *probable windellipse* is obtained by requiring half of the observations to lie within its dominion; we have then to determine c in such a way that

$$1 - e^{-c} = {}^1/_2 \quad , \quad c = 0.6932,$$

so that the axes of this ellipse are

$$\sqrt{2c} = \sqrt{2} \times 0.8326 = 1.177$$

times longer than those of the typical windellipse; the number 0.8326 is a quantity known in the theory of errors in the plane.

7. The frequency of the windvelocities, setting aside the direction, cannot be represented in a finite form; we can arrive at a form serviceable for comparison with the observation by writing (5) thus:

$$\frac{\sqrt{p^2-q^2}}{\pi} e^{-\mu} \cdot e^{-\nu R^2} \cdot e^{-R^2(\nu-p)+2R\lambda} R\, dR\, d\theta, \quad . \quad . \quad . \quad (8)$$

by developing the last exponential factor and then by expressing the powers and products of cosines in cosines of multiples.

It is clear that when integrating (8) with respect to θ from 2π to 0 only those terms are left which are independent of θ and which appear with the common factor 2π.

The expression to be found for the probability that a velocity lies between the limits R and $R + dR$ then becomes:

$$2\sqrt{p^2-q^2}\,.\,e^{-\mu}\,.\,e^{-pR^2}(1+a_1R^2+a_2R^4\;\ldots)\,R\,dR\,,\quad\ldots\quad(9)$$

where:

$$a_1 = s^2,$$

$$a_2 = q_2/2^2 \;+ qs^2/2!\;\cos 2\,(\varphi-\beta) + s^4/(2!)^2,$$

$$a_3 = q^2s^2/2^2 + qs^4/3!\;\cos 2\,(\varphi-\beta) + s^6/(3!)^2.$$

For Falmouth, where as was noticed above q can be put equal to nought these coefficients become simply:

$$a_n = s^{2n}\Big/\left(\frac{n!}{2}\right)^2,$$

and farther

$$s = pR_0\;,\;\mu = pR_0^2\;,\;\nu = p\;,\;\varphi = \alpha\;,\;\lambda = pR_0\cos(\theta-\alpha).\quad(10)$$

In practice it will frequently be only necessary to calculate a few of these coefficients; if we put:

$$q/p = \varepsilon,$$

the integration of (9) between the limits m and 0 leads to the expression:

$$\left.\begin{aligned}&\sqrt{1-\varepsilon^2}\,e^{-\mu}\times\\&(1-e^{-pm^2})\,.\left(1+\frac{a_1}{p}+\frac{2!a_2}{p^2}+\frac{3!a_3}{p^3}+\ldots\right)\\&-\frac{pm^2e^{-pm^2}}{1!}\left(\frac{a_1}{p}+\frac{2!a_2}{p^2}+\ldots\ldots\right)\\&-\frac{p^2m^4e^{-pm^2}}{2!}\left(\frac{2!a_2}{p^2}+\ldots\ldots\right)\end{aligned}\right\}\quad.\qquad(11)$$

As for $m = \infty$ this expression must become equal to unity, we have:

$$1+\frac{a_1}{p}+\frac{2!a_2}{p^2}\;\ldots\;=\frac{e^{\mu}}{\sqrt{1-\varepsilon^2}},$$

or, for the case $q = 0$, (11) becomes:

$$\left.\begin{aligned} & 1-e^{-pm^2} \\ & -\frac{pm^2e^{-pm^2}}{1!}(1-e^{-\mu}) \\ & -\frac{p^2m^4e^{-pm^2}}{2!}\left(1-e^{-\mu}-\frac{a_1}{p}e^{-\mu}\right) \text{ etc.} \end{aligned}\right\}, \quad . \quad . \quad . \quad (12)$$

from which is immediately evident that in many cases the three first terms are sufficient, so that then the calculation of the coefficients can be entirely avoided, or at most only a_1 must be taken into account; for generally μ is small, so that already

$$1-e^{-\mu}$$

will be a small quantity. If q is not small the calculation becomes rather tedious.

8. To find expressions for the quantities $\overline{V}$ and $\overline{V^2}$, the mean velocity and the mean square of the velocity independent of the sign, we have to multiply (9) successively by R and R^2 and to integrate between the limits ∞ and 0 which, with the well known fundamental equation, leads to the expressions:

$$\left.\begin{aligned} 1 &= A\left(1+\frac{2a_1}{2p}+\frac{2\,4a_2}{(2p)^2}+\frac{2.4.6a_3}{(2p)^3}+\ldots\right) \\ \overline{V} &= \frac{A}{2}\sqrt{\frac{\pi}{p}}\left(1+\frac{3a_1}{2p}+\frac{3.5a_2}{(2p)^2}+\frac{3.5.7.a_3}{(2p)^3}+\ldots\right) \\ \overline{V^2} &= \frac{2A}{2p}\left(1+\frac{4a_1}{2p}+\frac{4.6a_2}{(2p)^2}+\frac{4.6.8a_3}{(2p)^3}+\ldots\right) \\ A &= \sqrt{1-\varepsilon^2}\,e^{-\mu}. \end{aligned}\right\}. \quad (13)$$

9. For the calculation of the frequency of the directions independent of the velocity we have first to integrate (5) with respect to R between the limits ∞ and 0 and then with respect to θ between the desired limits θ; the mean velocity as function of the direction is found by the application of the same operation to (5) after multiplication by R. It is then easy to give to a frequency-formula found in this way the form of a FOURIER series. For brevity we treat here only the case that $q=0$ and the angle-limits are π to 0.

By putting

$$R=\varrho+\frac{\lambda}{\nu}$$

we get (5) reduced to the form:

$$\frac{\sqrt{p^2-q^2}}{\pi} e^{-\mu+\lambda^2/\nu} \int_{-\lambda/\nu}^{\infty} e^{-\nu\varrho^2} \left(\varrho + \frac{\lambda}{\nu} \right) d\varrho \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If $q = 0$, so that the formulae (10) hold good, we then find for the desired frequencies in the two easterly quadrants

$$\tfrac{1}{2} + \frac{1}{\sqrt{\pi}} \int_{0}^{R_0\sqrt{p}\,\sin\alpha} e^{-t^2}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

From this formula it is evident in what way and in what degree the asymmetry of the distribution is dependent of R_0, α and p.

10. The application of the given criteria has been made for Falmouth and the four seasons:

Winter: December, January, February, number 8384,

$p = 0.00258$, $q = 0.00004$

$R_0 = 5.22$, $\alpha = 222°8'$

Spring: March, April, May, number 8949,

$p = 0.00298$, $q = 0.00028$

$R_0 = 2.21$, $\alpha = 250°25'$

Summer; June, July, August, number 9229,

$p = 0.00485$, $q = 0.00029$

$R_0 = 5.60$, $\alpha = 251°22'$

Autumn: September, October, November, number 9254,

$p = 0.00313$, $q = 0.00004$

$R_0 = 3.80$, $\alpha = 239°16'$

For each series the number of observations is reduced to 10.000 and everywhere we have put $q = 0$, the calculated values are accordingly accurate as far as the fourth decimal.

In Table V we have compared the observed frequencies of wind-velocities independent of direction with those calculated according to formula (12), from which it is evident that the differences have a clearly systematic course. Just as is the case with all series of errors the number of the observed small velocities is larger than would agree with the normal distribution. The differences together amount in summer to about 10%, in winter to 15%.

In the calculation of the frequencies of the directions independent of the velocity, the observations regarded as calms — and to these are reckoned in the English records all velocities less than 4 miles an hour — have been distributed proportionally to the frequencies of direction; furtheron the frequencies North and South are assigned for one half to the eastern and western quadrants.

As is evident from the following table also in this comparison systematic differences appear; in all seasons the observed frequencies in the western quadrant are greater than the calculated ones, so that an increase of the constant part R_0 to which this uneven distribution can be attributed, would improve the correspondence.

TABLE VI.

Frequencies of winddirections at Falmouth

for 10.000 observations.

		Observed	Calculated	Difference
Winter	E. quadr.	3709	4006	— 297
	W. „	6291	5994	+ 297
Spring	E. quadr.	4037	4351	— 214
	W. „	5963	5649	+ 214
Summer	E. quadr.	2619	3009	— 390
	W. „	7381	6991	+ 390
Autumn	E. quadr.	3453	3980	— 527
	W. „	6547	6020	+ 527

TABLE V. Frequencies of windvelocities at Falmouth.
For 10.000 observations.

	WINTER			SPRING			SUMMER			AUTUMN		
Miles an hour	Observ.	Calculat.	Difference	Observ.	Calculat.	Difference	Observ.	Calculat.	Difference	Observ.	Calculat.	Difference
0 – 45	760	477	+ 283	756	569	+ 187	945	810	+ 135	936	588	+ 348
45– 95	1871	1482	+ 389	2073	1759	+ 314	2610	2336	+ 274	2126	1779	+ 377
95–145	1853	2026	– 173	2120	2279	– 159	2538	2728	– 190	2144	2304	– 160
145–195	1701	2030	– 329	1875	2120	– 245	1868	2133	– 265	1818	2110	– 292
195–245	1466	1650	– 184	1355	1558	– 203	1164	1225	– 61	1281	1564	– 283
245–295	967	1125	– 158	917	939	– 22	544	534	+ 10	792	920	– 128
295–345	680	656	+ 24	493	473	+ 20	224	178	+ 46	459	464	– 5
345–395	369	331	+ 38	250	201	+ 49	80	45	+ 35	258	179	+ 79
395–445	199	144	+ 55	114	72	+ 42	20	9	+ 11	116	66	+ 50
445–495	94	55	+ 39	31	22	+ 9	6	2	+ 4	37	20	+ 17
495–545	32	18	+ 14	15	6	+ 9	0	–	–	23	5	+ 18
545–595	8	5	+ 3	1	2	– 1	1	–	+ 1	10	1	+ 9
595–	–	1	– 1	–	–	–	–	–	–	–	–	–

Chemistry. — *"On the anisotropous liquid phases of the butyric ester of dihydrocholesterol, and on the question as to the necessary presence of an ethylene double bond for the occurrence of these phenomena"*. By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of February 23, 1907).

§ 1. In order to explain the behaviour of substances which are wont to exhibit double-refracting liquid phases, some investigators have started the hypothesis that, in this kind of organic substances, it might be a question of systems formed of two components, and of equilibrium phenomena between tautomeric and isomeric modifications, which would be converted into each other with finite velocity.

Although it is difficult to understand how such a supposition, which is easy to propound, but very difficult to prove, could explain the numerous well ascertained facts of the *regular* optical anisotropism of these phases, it might explain, however, at least to some extent, the peculiar irreversible transitions of phases, which I found more particularly with the esters of cholesterol and α-phytosterol, and also the hindrance phenomena noticed on that occasion [1]).

Such a supposition, however, is perhaps of some importance for the interpretation of the brilliant colour phenomena which accompany the phase-transitions in the cholesterol esters. For a mixture, or an emulsion of substances, whose indices of refraction differ very little, but whose dispersions differ much, might, like CHRISTHIANSEN's monochromes, cause a similar display of colours.

§ 2. There is more than one cause for tautomerism (or isomerism) in the case of these cholesterol esters, for all the esters, as well as cholesterol itself, possess an asymmetric carbon atom, and in solution they all polarise to the left.

Consequently, a racemisation during the esterification is by no means excluded, and we might, therefore, have a mixture of the optical antipodes. Cholesterol, moreover, possesses an ethylene double bond, so that we may also expect an isomerism in the sense of fumaric and maleic acids.

§ 3. As many other compounds (in fact most organic substances which are wont to exhibit these phenomena of doubly refracting

[1]) F. M. JAEGER, These Proc. 1906 p. 472 and 483 (29 December).

liquid phases) possess such ethylene double bonds, one might indeed imagine that the presence thereof in the molecule is of great importance for the occurrence of the said phenomena, if not the *conditio sine qua non*, as the structure of the azoxy-compounds is not yet firmly established and because it may be assumed that they contain, perhaps, similar double bonds between *N* and *O*.

Moreover, the cholesterol esters all contain *three* liquid phases, so that this peculiar complication might perhaps also be connected with the possibility of very intricated isomerism-phenomena of those substances.

§ 4. In order to answer these questions, I asked Prof. Dr. C. NEUBERG of *Berlin* to furnish me with a specimen of his synthetic *Dihydrocholesterol*, to which request this savant most willingly acceded.

I wish to thank Prof. NEUBERG once more for his kindness.

In this *Dihydrocholesterol* the ethylene double bond has disappeared owing to the addition of two atoms of hydrogen, and the malenoid and fumaroid isomerism is therefore, à priori excluded.

§ 5. I have prepared from this alcohol the acetic and the normal butyric esters, by means of the pure acid-anhydrides, and have examined the same as to their phase transitions. The acetic ester will be described elsewhere later on; here the butyric ester only will be discussed.

As a highly important result I may mention that the colour phenomena on melting and the occurrence of three liquid modifications in the normal butyrate remain unaltered as before, but that the irreversibility of the phase-transitions is shown in a manner just the reverse as in the case of most of the cholesterol esters, e.g. the laurate.

Whereas of the two doubly-refracting liquid phases of the last named substance, one is always passed over *on cooling*, whilst both are found *on melting* the solid substance, this is just the reverse in the case of the dihydrocholesterol-*n*-butyrate.

6. The solid phase *S* consists of an aggregate of very thin, colourless, and clear transparent laminae in which the plane of polarisation makes an obtuse angle with the sides of demarcation and exhibit in convergent polarised light a hyperbole with very strong colour dispersion $\varrho > v$.

On heating, this phase *S* passes into a doubly-refracting liquid *B*, consisting of very small, feebly doubly-refracting individuals, which in turn passes at a higher temperature into the isotropous fusion *L*.

Of colour phenomena during one of these transitions, absolutely *nothing* is noticed.

If, however, we start from the phase L and allow the same to cool, we first notice the doubly-refracting phase B, which on further cooling, amid violent sudden currents of the mass, passes into a much more strongly doubly-refracting liquid A, which on continued cooling crystallises suddenly, also amid very violent currents, to an aggregate of flat needles, glittering in vivid interference colours. These in turn, rapidly assume a spherolite structure so that the solid phase S itself appears to be also *dimorphous* and *monotropous*, as the flat needles are *not* reobtained on warming the spherolitic mass. The transformation of A into these needles, during cooling, is accompanied with the most vivid display of colours. Under the microscope these may be recognised by the dark-green colour of the background of the field of vision; with the naked eye, however, with incident light, that colour-display commences with a brilliant violet gradually turning into blue and finally into a radiating green when the mass crystallises. I have never noticed red or yellow colours with incident light. These phenomena return in the same order when the experiment is repeated.

That the phase A really exhibits the behaviour of a stable phase

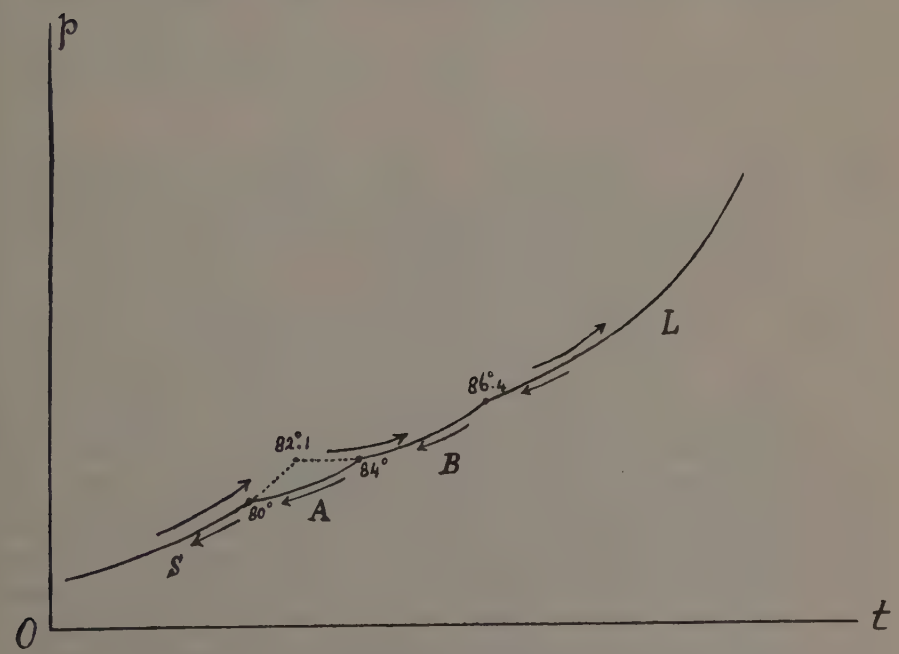


Fig. 1.
Schematic p-t-diagram for Dihydro-cholesterol-n-butyrate.

is also shown by the fact that, the colour having become blue or green on cooling, turns again violet on warming, so long as the solid phase S has not yet been attained. The phase is, therefore, realisable at a change of temperature in *two* directions.

§ 7. As I had but very little of the substance at my disposal, the thermometric determinations could only be studied in capillary tubes with the aid of a magnifying glass.

At 82.°1 the phase S melts to a doubly-refracting phase B which becomes clear at 86.°4 and passes into L. On cooling this isotropous fusion, it first passes properly into B at 86°.4, but at 84° into the more strongly doubly-refracting phase A, which may be undercooled many tens of degrees, and with retention of its violet colour, before passing into the solid phase S.

Want of material prevented my determining the true solidifying point of S by inoculation; I estimate it at about 80°.

Thus the positive proof has been given that the remarkable colour phenomena accompanying the melting the cholesterol esters *cannot* be attributed to the presence of an ethylene double bound; also that an eventual presence of fumaroid and maleinoid isomers cannot be considered as the cause of the occurrence of the *three* liquids.

Zaandam, 15 Febr. 1907.

Chemistry. — "*On the action of bases, ammonia and amines on s. trinitrophenyl-methylnitramine.*" By Prof. P. VAN ROMBURGH and Dr. A. D. MAURENBRECHER.

(Communicated in the meeting of February 23, 1907).

s.-Trinitrophenyl-methylnitramine, as has been known for a long time, is decomposed at the ordinary temperature by ammonia in alcoholic solution, or on warming, by an aqueous solution of potassium hydroxide, or carbonate, in the first case with formation of picramide, in the second (with evolution of monomethylamine) of picric acid. One of us who formerly studied the reaction with bases concluded, from the occurrence of the amine and the formation of nitric acid which was also observed, that the methylnitramine which might be expected according to the equation :

$$C_6H_2(NO_2)_3 \cdot \underset{\underset{NO_2}{|}}{N}\text{-}CH_3 + KOH = C_6H_2(NO_2)_3 \cdot OK + \underset{\underset{NO_2}{|}}{HN}\,CH_3$$

might have become decomposed [1]).

From the reaction of methylamine on tetranitrophenyl-methylnitramine and on trinitromethylamidomethylnitramidobenzene he afterwards concluded [2]) that, probably, there had been formed methylnitramine, meanwhile discovered by FRANCHIMONT and KLOBBIE [3]).

The amount of amine formed by the decomposition of trinitrophenyl-methylnitramine by alkalis is considerably smaller than might be expected from theory; the possibility, therefore, exists that the reaction proceeds indeed mainly in the above indicated sense.

We have, therefore, taken up the problem again in the hope that by suitable modifications in the reaction, we might get at a process for the preparation of methylnitramine which would have the advantage of yielding this costly substance from a cheap, easily accessible material. We were not disappointed in our expectations.

If trinitrophenyl-methylnitramine, which is the final product of the nitration of dimethylaniline and melts at 127°, is boiled with a 10% solution of potassium carbonate a brownish-red solution is obtained, which on cooling gives an abundant deposit of potassium picrate. If after filtration the liquid is acidified with sulphuric acid and again filtered off from the picric acid precipitated and then agitated with ether, the latter yields on evaporation crystals, which after purification, melt at 38°, and are identical with methylnitramine, as was proved by comparing the compound with a specimen kindly presented to us by Prof. FRANCHIMONT. The yield, however, was very small.

If the finely powdered nitramine, m. p. 127°, is treated with 20% methylalcoholic ammonia this becomes intensely red, the mass gets warm and after a few hours the reaction is complete, and a large amount of picramide has formed which is removed by filtration. The alcoholic solution is distilled in vacuo, the residue treated with dilute sulphuric acid and, after removal of a yellowish byeproduct by filtration, the liquid is agitated with ether. On evaporation of the ether, crystals of methylnitramine were obtained. In this reaction also, the yield was not large, amounting to only 15% of the theoretical quantity. With ethyl-alcoholic ammonia a similar result was obtained, whereas an experiment in which ammonia was passed into a solution

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[1]) Rec. d. Trav. chim. d. Pays-Bas, II. (1883) p. 115.

[2]) Ib. VIII (1889) p. 281.

[3]) Ib. VII (1888) p. 354.

of the nitramine in benzene gave results which were still less favourable.

One of us had noticed previously that among the aromatic amines which generally react on an alcoholic solution of the nitramine quite as readily as on picryl chloride, *p*-toluidine in particular gives a beautifully crystallised *p*-toluylpicramide m. p. 166° [1]) whilst the alcoholic solution contains only comparatively few, not very dark coloured byeproducts. In an experiment in which 35 grams of the nitramine were heated on the waterbath with an equal weight of *p*-toluidine and 100 c.c. of 96 % alcohol, a fairly violent reaction set in after some time. The heating was continued for 5 hours and, after the picramide derivative had been removed by filtration, the alcohol was distilled off and the residue extracted with dilute sulphuric acid. The liquid filtered off from the toluidine sulphate was shaken with ether. On evaporation of the ether a still yellow coloured liquid product was left which on being inoculated with a crystal of methylnitramine became crystalline and after having stood for some time over sulphuric acid weighed 7 grams. On pressing between filter paper light yellow crystals were obtained which after being sublimed in vacuo (a treatment which methylnitramine stands very well) melted at 38°. On mixing the same with a preparation consisting of pure nitramine the melting point was not affected.

p-Toluidine appears, therefore, to be a suitable means for readily procuring in a short time methylnitramine from *s*-trinitrophenylnitramine.

We are continuing our investigations with different amines and also with other nitrated aromatic nitramines, and will state the results more elaborately in the "Recueil".

Org. Chem. Lab. of the University *Utrecht.*

Physics. — "*Wave-lengths of formerly observed emission and absorption bands in the infra-red spectrum.*" By Prof. W. H. JULIUS.

If in the infra-red spectrum, as formed by means of a rock-salt prism, the positions of emission or absorption bands have been carefully determined, the corresponding wave-lengths still are uncertain by an amount which, in a considerable part of the spectrum, is greater than the probable error of those determinations, because the

[1]) We now obtained this substance in two modifications, one coloured dark red and the other orange.

dispersion curve of rock-salt is not yet known with sufficient exactness.

Mr. W. J. H. MOLL [1]) has lately compared with each other the dispersion curves that have been calculated according to KETTELER's formula with two sets of constants, one given by RUBENS [2]), the other by LANGLEY [3]). LANGLEY's results held for a temperature of 20°; the numbers given by RUBENS were corrected by Mr. MOLL so as to apply to the same temperature. While coinciding in the visible spectrum, the two dispersion curves appeared to diverge very sensibly in the entire infra-red region, the wave-lengths corresponding to given indices of refraction being smaller with RUBENS' than with LANGLEY's constants. At $\lambda = 1{,}5\ \mu$ e. g. the difference amounts to $0{,}028\ \mu$; it increases unto $0{,}062\ \mu$ (at $\lambda = 3\ \mu$) and then decreases to $0.032\ \mu$ (at $\lambda = 8{,}5\ \mu$). If, on the other hand, the indices of refraction, which according to LANGLEY's and according to RUBENS' formula belong to rays of given wave-lengths, be compared with each other, the difference appears to be rather constant between $\lambda = 4\ \mu$ and $\lambda = 8{,}3\ \mu$, namely 1,5 units of the 4th decimal of the index, and to increase from 0 to 1.5 similar units in the region between $0.6\ \mu$ and $4\ \mu$.

The apparatus, nowadays available for the investigation of the infra-red, admit of determining the position of sharp maxima or minima of radiation with an accuracy, going a good deal farther than 1,5 units of the 4th decimal of the index.

When between 1887 and 1891 I investigated several infra-red emission and absorption spectra, our knowledge of the dispersion of rock-salt was restrained to the outcome of LANGLEY's first determinations [4]), which extended only as far as $5{,}3\ \mu$. As a great part of my work bore upon longer waves, I published my results in the form given by direct observation, viz, as galvanometer deflections and corresponding angles of minimum deviation, reduced to the temperature 10°. The refracting angle of the prism being also recorded, the indices of refraction of rock-salt for waves, corresponding to the observed maxima, were thus implicitly given.

In order to obtain a rough estimate of the wave-lengths, I had extended LANGLEY's dispersion curve in a straight line, though under strict reservation. The wave-lengths as read on this lengthened

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1) W. J. H. MOLL, Onderzoek van ultra-roode spectra. Dissertation, Utrecht, 1907.

2) H. RUBENS, Wied. Ann. 60, 724; 61, 224; 1897. Cf. also KAYSER, Handbuch der Spectroscopie I, 371, 1900.

3) S. P. LANGLEY, Ann. Astroph. Obs. of the Smiths. Inst. I, 1900.

4) S. P. LANGLEY, Phil. Mag., Aug. 1886.

curve, to which I myself assigned little weight [1]), have found their way to some text-books [2]), where they unfortunately appear as the results of my investigation, with the incidental remark that they are incorrect, as founded on a false extrapolation. It is clear, however, that this incorrectness has nothing to do with the accuracy with which the position of the bands in the prismatic spectrum has been determined. Now I have reason to believe, that the spectrometric and heat-measuring apparatus used in that research were not less valid than those employed by many later observers of infra-red spectra (DONATH, PUCCIANTI, IKLÉ, COBLENTZ, NICHOLS, RUBENS and ASCHKINASS and others), so that the results still retain their value as a first contribution to our knowledge of the examined spectra.

I therefore thought it suitable to republish the principal results obtained at that time [3]), but now to mention the indices of refraction for the maxima of emission and absorption, as following directly from my observations, and to add the wave-lengths, as derived from the more recent dispersion curves of RUBENS and of LANGLEY.

The positions in the infra-red were determined in my work with respect to the place of the *D*-lines of a BUNSEN flame coloured with chloride of sodium. But the latter were too faint to be observed with the bolometer; and the transition from the visual observation of the *D*-lines to the bolometric observation of infra-red radiations caused an uncertainty in the determination of the relative positions, which was still increased through the necessity of displacing the bolometer along the optical axis of the rock-salt lens according to its different focus for visible and invisible rays. It was chiefly in the part of

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[1]) Cf. „Bolometrisch onderzoek van absorptie spectra", Verhandelingen der Kon. Akad. v. W. te Amsterdam, Vol I, N°. 1, p. 8 (1892), or the German translation in: Verhandl. des Vereins zur Beförderung des Gewerbfleisses, 1893, p. 235, where I have clearly stated that I considered the extrapolation of LANGLEY's dispersion curve as quite uncertain, and that in the tables the direct data of observation (angles of minimum deviation) were given, because I did not like to have my results inseparably connected with a possible incorrectness of the dispersion curve. The passage in question seems not to have been noticed by W. W. COBLENTZ, for in his excellent work "Investigations of Infra-red Spectra", published by the Carnegie Inst. of Washington, 1905, he says on p. 135, after alluding to LANGLEY's extrapolation of the dispersion curve in a straight line: "JULIUS, with apparently less hesitation, has applied this extrapolation to his work".

[2]) WINKELMANN, Handbuch der Physik; KAYSER, Handbuch der Spectroscopie; CHWOLSON, Lehrbuch der Physik.

[3]) Recherches bolométriques dans le spectre infra-rouge. Arch. neérl. **22**, p. 310—383 (1888).

Die Licht- und Wärmestrahlung verbrannter Gase, Berlin, Simion. 1890.

Bolometrisch onderzoek van absorptiespectra, l. c.

the investigation, described on p. 69 of "Die Licht und Wärmestrahlung verbrannter Gase" that many pains were taken to reduce this source of error. There the CO_2-maximum of the BUNSEN flame was found at minimum deviation 38°54′20″, the refracting angle of the prism being 59°53′20″ and the temperature 10°. From this follows $n = 1{,}52103$. Had the temperature been 20°, then the deviation would have been found smaller by 1′50″, giving for the index of refraction: $n = 1.52069$.

If we suppose this value to be exact, then the angles of minimum deviation given in my first paper in Arch. néerl. 22, and on pages 47—68 of "Die Licht- und Wärmestrahlung" are too small by nearly 3′, owing to an instrumental error. In "Bolometrisch onderzoek van absorptiespectra" the deviation of the CO_2-maximum has been found 38°52′40″ instead of 38°54′20″; 1′ of this difference results from the fact that the refracting angle of the prism, then in use, was smaller than that of the other one by 1′; only the remaining 40″ were owing to an instrumental error.

I have now applied the corrections resulting from this re-examination, and calculated the indices of refraction for 20°, the temperature to which the dispersion curves as compared by Mr. MOLL also refer. In finding the wave-lengths corresponding to the indices, advantage has been taken of elaborate tables, prepared by Dr. MOLL for a research of his own, and which he was kind enough to put at my disposal.

Emission-spectrum of:	Indices of refraction for the maxima (Temp. 20°)		Wave-lengths according to the dispersion curve of RUBENS	of LANGLEY	Intensity [1]
BUNSEN-flame	1.5268		1.905	1.953	0.5
	1.5247	H_2O	2.769	2.831	3—5
	1.52069	CO_2	4.410	4.462	10
Flame of carbon monoxyde	1.52445	CO_2	2.883	2.947	1
or of cyanogen	1.52069	CO_2	4.410	4.462	10
Hydrogen flame	1.5247	H_2O	2.77	2.83	10
	1.5176		5.41	5.46	2
Luminous gasflame. . .	1.5270	C	1.84	1.89	[2]
	1.5247	H_2O	2.77	2.83	[2]
	1.5207	CO_2	4.41	4.46	[2]
Hydrog. burning in chlor.	1.5226	HCl	3.68	3.74	
Flame of sulfur	1.5093	SO_2	7.49	7.52	
Flame of carb. disulphide	1.5247		2.77	2.83	1
	1.5207	CO_2	4.41	4.46	10
	1.5125	COS(?)	6.76	6.80	3—0 [2]
	1.5093	SO_2	7.49	7.52	2—3 [2]
Absorption-spectrum of:					
C (diamond)	1.5238		3.18	3.24	
	1.5202		4.58	4.63	10
	1.5183		5.20	5.25	
	1.5088 etc. [3]		7.59	7.62	10
H_2O	1.5287		1.41	1.43	1
	1.5265		2.01	2.06	1
	1.5236		3.25	3.31	9 s
	1.5194		4.85	4.90	
	1.5146		6.24	6.28	

[1]) In each spectrum the intensity of the highest maximum is indicated by 10. The letter s following an intensity figure means, that the band is rather sharp.

[2]) The relative intensity of these bands varies much with the place in the flame.

[3]) The addition "etc." behind an index of refraction indicates, that the band marks the beginning of an extensive region of strong absorption.

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lenghts according to the dispersion curve of RUBENS	of LANGLEY	Intensity
CS_2	1.5203	4.55	4.60	6 s
	1.5129	6.67	6.71	10
$S_2 Cl_2$	1.5219	3.96	4.02	1
	1.5163	5.78	5.82	1
	1.5090	7.55	7.58	7 s
	1.5049	8.36	8.39	1
	1.5020	8.90	8.93	1
	1.4992	9.41	9.44	8 s
	1.4942	10.28	10.31	10
PCl_3	1.5221	3.88	3.94	0.5
	1.5082	7.72	7.75	10 s
	1.5030	8.73	8.76	0.5
	1.4944	10 25	10 28	10
$Si Cl_4$	1.5172	5.53	5.57	6 s
	1.5154	6.03	6.07	1
	1.5058	8.19	8.22	10 s
	1.5014	9.02	9.05	10
	1.4974	9.73	9.76	10
$Si HCl_3$	1.5234	3.34	3.40	0.5
	1.5173	5.50	5.54	1 s
	1.5058	8.19	8.22	3
	1.5014	9.02	9.05	10
	1.4974	9.73	9.76	3
$C Cl_4$	1.5137	6.47	6.51	9 s
	1.5058	8.19	8.22	10 s
	1.4942	10.28	10.31	5 s
$C H Cl_3$	1.5234	3.34	3.40	3
	1.5131	6.62	6.66	3 s
	1.5115	6.99	7.03	4
	1.5058	8.19	8.22	10
	1.4980	9.62	9.65	7

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve of RUBENS	Wave-lengths according to the dispersion curve of LANGLEY	Intensity
$CHBr_3$	1 5235	3.30	3.36	3 s
	1.5207	4.40	4.45	3 s
	1.5164	5.76	5.80	4 s
	1 5116	6.97	7 01	3
	1.5083	8.19	8.22	7 s
	1.5024	8.83	8.86	10
	1.4992	9.41	9.44	6
C_6H_6	1.5259	2.25	2.31	1
	1.5236	3 25	3.31	4 s
	1.5211	4.26	4.31	1
	1.5173	5.50	5.54	6 s
	1.5128	6 69	6.73	10 s
	1.5107	7.18	7.21	3 s
	1.5088	7.59	7.62	1
	1.5060	8.15	8.18	2
	1.5039	8.56	8.59	7
$(C_3H_7)_2$	1.5259	2.25	2.31	2
	1.5230	3.51	3.57	7 s
	1.5154	6.03	6.07	1
	1.5118	6.93	6.96	10 s[1])
	1.5097	7.40	7.43	6
	1.5068	7.99	8.02	4
	1 5032	8.69	8.72	6 s
	1.4980	9.63	9.66	5
	1.4942	10.28	10.31	5
CH_3OH	1.5259	2.25	2.31	1
	1.5229	3.56	3.62	10
	1 5194	4 85	4.90	2 s
	1.5145 etc.	6.27	6.31	10
C_2H_5OH	1.5259	2.25	2.31	1
	1 5229	3.56	3.62	10
	1.5183	5 20	5.25	2 s
	1.5154	6.03	6.07	2
	1.5126 etc.	6.74	6.78	10

[1]) Sharply limited only toward the smaller wave-lengths.

Absorption-spectrum of:	Indices of refraction for the maxima (Temp. 20°)	Wave-lengths according to the dispersion curve of RUBENS	Wave-lengths according to the dispersion curve of LANGLEY	Intensity	
C_3H_7OH	1.5230	3.51	3.57	10	
	1.5152	6.09	6.13	3	
	1.5126 etc.	6.74	6.78	10	
C_4H_9OH (normal). . . .	1.5230	3.51	3.57	10	
	1.5162	5.81	5.85	3	
	1.5126 etc.	6.74	6.78	10	
C_4H_9OH (iso).	1.5230	3.51	3 57	10	
	1.5192	4.92	4.97	1	
	1.5154	6.03	6.07	2	
	1.5126 etc.	6 74	6.78	10	
$C_5H_{11}OH$.	1.5230	3.51	3.57	10	
	1.5192	4.92	4.97	1	
	1.5154	6.03	6.07	3	
	1.5126 etc.	6.74	6.78	10	
$(C_2H_5)_2O$.	1.5327	0.953	0.958	1	
	1.5293	1.30	1.32	1	
	1.5259	2.25	2.31	2	
	1.5230	3.51	3.57	8	s
	1.5183	5.20	5.25	3	s
	1.5164	5.76	5.80	1	
	1.5116	6.97	7.01	10	
	1.5099	7.35	7.39	4	
	1.5078	7.80	7.83	4	s
	1.5045 etc.	8.44	8.47	10	
C_2H_5SH	1.5256	2.38	2.44	1	
	1.5230	3.51	3.57	5	
	1.5221	3.88	3.94	3	
	1.5183	5.20	5.25	1	
	1.5162	5.81	5.85	1	
	1.5115	6.99	7.03	10	
	1.5074	7.88	7.91	10	
	1.5001	9.25	9.28	8	
	1.4936	10.39	10.42	9	

Physics. — "*A hypothesis relating to the origin of* RÖNTGEN-*rays.*" By Prof. C. H. WIND.

W. WIEN [1]) has measured the energy of RÖNTGEN-rays, converted into heat in a bolometer or in a thermo-element, and has compared it with that of the cathode-rays, likewise converted — with exception of the small fraction transformed in energy of R.-rays — into heat in the anti-cathode. He finds for the proportion of the total quantities of energy of the two kinds of rays

$$\frac{E_r}{E_k} = 2{,}18 \;.\; 10^{-3}\ ^{2}).$$

Supposing that the R.-rays are the radiation of energy, emitted by cathode-ray electrons being brought to rest, and that this stoppage may be considered as a continually decreasing motion, he proceeds with the aid of the theory of M. ABRAHAM to deduce the duration of the stoppage and from it the thickness of the R-waves. For the latter he finds

$$\lambda = 1{,}15 \;.\; 10^{-10} \text{ cm.}$$

Results of the same order of magnitude have afterwards been attained by EDNA CARTER [3]) in an investigation, also made at the laboratory directed by WIEN.

These results do not very well agree with the values, derived by HAGA and myself for the wave-length of R.-rays from diffraction-experiments:

$$\lambda = 270 \text{ to } 12 \;.\; 10^{-10} \text{ cm } ^{4})$$

and

$$\lambda = 160 \;,\; 120 \;,\; 50 \;.\; 10^{-10} \text{ cm. } ^{5})$$

If the R.-rays have to be considered as disturbances in ether of the single pulse character assumed by WIEN in accordance with the current conception, the same numbers must be divided by $\frac{3.7}{1\frac{1}{9}}$ or $2\frac{1}{2}$ [6]) in order to represent the corresponding values of the thickness of the pulse-waves, which consequently become

$$\beta_1 = 110 \text{ to } 5 \;.\; 10^{-10} \text{ cm,}$$
$$\beta_2 = 64,\ 48,\ 20 \;.\; 10^{-10} \text{ cm.}$$

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[1]) W. WIEN. WÜLLNERS Festschrift, Leipzig, 1905; Ann. d. Ph. 18, p. 991, 1905.

[2]) L. c. p. 996. The number is doubled here, on account of the remark made regarding it on page 1000.

[3]) E. CARTER. Ann. d. Ph. 21, p. 955, 1906.

[4]) H. HAGA and C. H. WIND. These Proc. I. p. 426.

[5]) Id. Ibid. V. p. 254.

[6]) C. H. WIND. Physik. Zschr. 2, p. 96. Fussnote 2), 1901.

WIEN's experiments would have led to results more in keeping with the diffraction experiments, if the values found for the energy of the R.-rays had been 20 to 100 times smaller. The difference is too great to ascribe it to errors of observation. We must rather think of fundamental errors in the method of observation or of a viciousness in our conceptions concerning the mechanism of the phenomena.

As for the method of observation WIEN himself pointed out[1]) the possibility that the quantity of heat, generated in the bolometer or in the thermo-element, should not be to its full amount converted energy of R.-rays, but partly also — perhaps even for the greater part — converted atom-energy, liberated by a, say, catalytic action of the R.-rays.

J. D. v. d. WAALS Jr.[2]) suggests the additional idea that the electrons are not generally stopped at once by a simple uniform decrease of velocity, but will mostly, by their interacting with the particles of the anti-cathode, before being brought to rest move for some time amidst the latter in rapidly changing directions with great velocities, sending out a new R.-pulse at every change of motion. Starting from this idea we could, indeed, expect from each electron a much greater contribution to the energy of radiation than in the theory accepted by WIEN and find the results of WIEN's energy-measurements in better agreement with those of the diffraction-experiments.

Nevertheless it seems to me that by the side of this another idea deserves our attention, which might be more in keeping with the properties of cathode-rays as far as known. It would be this, *that not simply the cathode-ray electrons, but in combination with these the atoms of the anti-cathode are the principal centres of emission of R.-rays.*

It should be imagined, that the electrons, arriving at the anticathode with their immense velocities, are not, generally, thrown into an other direction by the atoms, but will for the greater part pass straight through them, and even, in doing so, will mostly not suffer any persisting decrease of velocity. This idea is by no means a new one. It has been worked out by LENARD[3]), who sees in it the best explanation for the laws of absorption of the cathode-rays. In very few cases only it will happen that an electron, when piercing an atom, gets imprisoned

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1) W. WIEN. Drudes Ann. d. Ph. 18, p. 1005, 1905; cf. also E. CARTER. Ann. d. Ph. 21, p. 957, 1906.

2) J. D. v. d. WAALS JR. Ann. d. Ph. 22. p. 603. 1907.

3) P. LENARD. Drudes Ann. d. Ph. 12, p. 734, 1903.

or changes its direction considerably [1]) in a centre of exceedingly strong electromagnetic action; in the great majority of cases it will, by the abundance of vacant space in the interior of the atom [2]), fly across it without experiencing a considerable decrease of velocity.

In this way the greater part of the electrons will pierce thousands or tens of thousands of atoms before being stopped, and we find easily explained the great penetrating power of the cathode-rays, which may still in appreciable quantity pass through a layer of aluminium $10\,\mu$ [3]) thick or a layer of atmospheric air, some cm thick [4]).

If we consider the values given by the diffraction-experiments for the order of magnitude of the thickness of R.-waves as correct, it follows from WIEN's experiments — apart from a possible catalytic action of the R.-rays — that the radiation of the cathode-ray corpuscles, by the simple fact of their stoppage, could account only for something like $\frac{1}{20}$ or $\frac{1}{100}$ of the whole energy of the R.-rays. Consequently for by far the greater part this energy must, if LENARD's views may be accepted, have a different origin. What this can be, is obvious. The atoms namely will by no means remain undisturbed during the sudden passage of an electron. Themselves probably consisting of negative and positive corpuscles, they will see their electromagnetic fields during the passage altogether altered and at the same time will no doubt send out a pulse or wave of disturbance [5]) into the surrounding ether. About the character or shape of these pulses, which moreover may vary from one case to an other, we can, without making any more definite assumptions as to the structnre of the atom, say little; but there is one important point, in which all these pulses will be to a certain degree similar, viz. their *duration*.

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[1]) Together with the expulsion of electrons originally belonging to the atom, which will often occur at the same time, these changes of direction could very well account for the diffusion of the cathode-rays according to LENARD.

[2]) LENARD calculates (Drudes Ann. d. Ph. 12, p. 739, 1903) that only 10^{-9} of the volume of an atom is occupied by the "dynamids", of which he considers it to consist.

[3]) LENARD. Wied. Ann. 51, p. 233, 1894.

[4]) Id., Ibid., p. 252.

[5]) LENARD expresses himself ("Ueber Kathodenstrahlen", Nobel-vorlesung, p. 37, Leipzig 1906) as follows: "Das durchquerende Strahlenquant" — the electron — "wird vermöge der abstossenden Kräfte, welche es auf die anderen, dem Atom eigenen, negativen Quanten ausübt, eine gewaltige Störung innerhalb des Atoms hervorbringen können", and then continues thus: "und als Folge dieser Störung kann ein dem Atom gehöriges Quant aus ihm hinausgeschleudert werden (sekundäre Kathodenstrahlung)"; but he does not speak of a radiation emitted by the atom.

The latter will be, if a represents the diameter of an atom and v the velocity of the electron, which is piercing it, something like (rather smaller than) $\frac{a}{v}$, causing the wave emitted to be of a thickness of something like (rather smaller than) $c\,\frac{a}{v}$, c being the velocity of light in ether. By putting $a = 10^{-8}$ and $v = 10^{10}$, we get by this way for $c\,\frac{a}{v}$ 3.10^{-8}, a number which only slightly exceeds the order of magnitude of the values of β (p. 714), derived from diffraction experiments. It might therefore be possible, *that the waves of disturbance in question should be identical with the Röntgen rays.*

As by this theory a single electron would disturb some thousands or tens of thousands of atoms, every atom, being traversed by an electron, need only send out something like $\frac{1}{100}$ of the quantity of energy emitted by an electron itself in its total stoppage, in order to account for the relatively large amount of energy found by WIEN in the R-rays. That such proportions should exist, seems to me not impossible at all.

The views presented here as to the origin of the R.-rays bestow a new and great importance on the "wave-length" of these rays, as they intimately connect this measurable quantity with the dimensions of the atoms. Whether there really exists such a close connection, could perhaps be experimentally put to the test by diffraction experiments with anticathodes made from different materials. More generally it might be expected that experiments of this kind would throw some new light upon the structure of atoms, and also of molecules or molecule aggregates. In such experiments it would certainly have a peculiar interest to use crystals as anticathodes, as perhaps the regular structure of these bodies could manifest itself both in rather sharply defined wave-lengths of the R.-rays emitted by them as in a polarisation of these rays.

The question, whether R.-rays should or should not be expected to show total or partial polarisation, may be treated on the basis of the above hypothesis, as soon as this be supplemented by definite suppositions about the structure of the atom.

The relation that, according to our views, should have to exist between the wave-length of R.-rays and the velocity of the cathode-rays, is of course liable to rather direct experimental verification.

Two further questions connected with those views and perhaps liable also to be answered by way of experiment, are these:

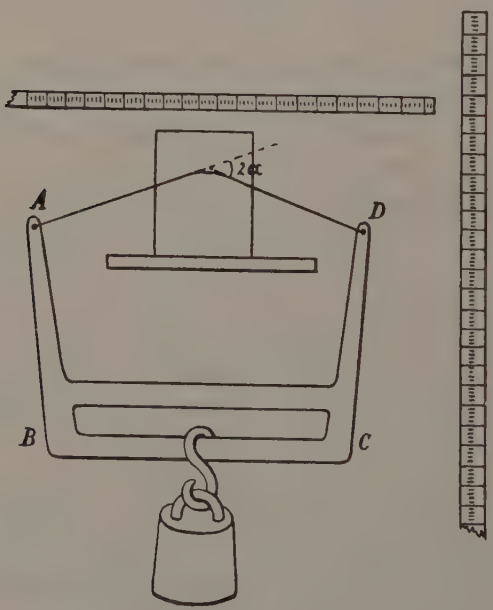
1. whether the air molecules on the outside of the aluminium window of LENARD emit R.-rays in appreciable quantity;

2. whether the γ-rays of a radio-active substance, except by the substance itself, are to a considerable extent emitted also by the atoms of air in its neighbourhood on their being pierced by the electrons constituting the β-rays.

Physics. — "*On the motion of a metal wire through a piece of ice.*" By Dr. J. H. MEERBURG. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of January 26, 1907).

During the last and the preceding winter I made some measurements with a purpose of testing the formulae, expressing the velocity of descent of a metal wire through a block of ice, which Mr. L. S. ORNSTEIN had derived from the theory of regelation [1]).



In my experiments the metal wire was fastened at both ends to

[1]) L. S. ORNSTEIN. These Proc. VIII, p. 653.

the legs A and D of an iron frame, which, in order to secure greater rigidity, had been cut from an iron plate. In the first measurements the downward displacements of the wire were observed by means of a small reading telescope, turning round a horizontal and a vertical axis, and were determined on a measuring rod, mounted at the side of the frame. The breadth of the ice-block was also read on a horizontal measuring rod. In the later experiments a cathetometer was used, placed at my disposal by the professors of the Technical University at Delft. I wish to express here my sincere thanks to these gentlemen, especially to Prof. DE HAAS. The fall of the wire was always derived from the change in the difference of level between the top of the wire and the upper edge of a small bubble, existing somewhere in the interior of the ice. Every ten minutes or, when the descent was quicker, every five minutes, the difference of level was measured in order to ascertain whether the fall was regular. Each experiment lasted 20 to 40 minutes.

The ice used was artificial commercial ice. From a larger block a clear smaller one was sawn out, in which some bubbles should be present to serve as marks. The faces were melted flat by pressing them against a metal plate, so that errors, caused by irregular refraction, were avoided.

Heat conduction along the wire was prevented by hanging small pieces of ice on the wire on both sides of the block. Still small grooves were occasionally formed when the descent was slow.

The experiments were made with wires of steel, german silver and silver. The thickness of the wires was measured by means of caliber compasses, giving results accurate to 0.01 mm. The thickness was 0.5, 0.4 and 0.3 mm. Deviations from these numbers, amounting to some hundredths of a millimetre, were occasionally found.

For the case, realised in my experiments, in which the two straight ends of the wire make a certain angle 2α with each other, formula (IIIa) of Mr. ORNSTEIN's paper [1]) holds:

$$v = \frac{2\alpha CP}{d_1 \sin \alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which v represents the velocity of descent of the wire, P the total weight and d the breadth of the ice-block. C is a constant. The value of this constant I calculated by formula (1) from the values of v, found in my experiments.

The results are summarised in the following table:

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1) l. c.

	P (in grammes).	C	average of C.
Steel wire.		Diameter 0.5 mM.	
	455	0.0162	0.017
	755	0.0151	
	1255	0.0172	
	2160	0.0185	
	2205	0.0169	
	5160	0.019	
		diameter 0.4 mM.	
	455	0.030	0.029
	755	0.029	
	1255	0.029	
		diameter 0.3 mM.	
	755	0.043	0.0425
	1255	0.042	
German silver.		diameter 0.5 mM.	
	755	0.0134	0.014
	1255	0.0119	
	2150	0.0143	
	5160	0.0172	
		diameter 0.4 mM.	
	755	0.0196	0.022
	1255	0.0204	
	2150	0.0208	
	5160	0.0255	
		diameter 0.3 mM.	
	555	0.0306	0.035
	755	0.0348	
	855	0.0393	
Silver wire.		diameter 0.5 mM.	
	755	0.0207	0.023
	1255	0.0255	
		diameter 0.4 mM.	
	536	0.0367	0.039
	755	0.0384	
	1036	0.0392	
	1255	0.0404	
		diameter 0.3 mM.	
	555	0.0347	0.041
	755	0.0467	

The quantity C is not expressed here in C.G.S. units, since the dimensions have been taken in millimetres, the velocities in millimetres per minute and the forces in grammes. In order to reduce them to C.G.S. units, the value of C has to be multiplied by 170×10^{-9}.

The values given in the table are averages of several measurements. In order to show the deviations of different measurements, made with the same weight, I give here an arbitrarily chosen set of separate measurements.

German silver wire, diameter 0.4 mm.

Number of the experiment	P	v	d_1	2α	C	averages.
8	1036	1.017	39.0	42°	0.0368	
10	1036	1.11	37.4	42°	0.0393	0.0392
14	1036	1.27	35.4	37°	0.0411	
17	1036	1.73	29.3	30°	0.0393	
87	1255	0.99	52.3	50°	0.0401	
112	1255	1.09	51.27	53°	0.043	0.0404
115	1255	0.756	66.46	53°	0.0387	

The value of C is calculated by Mr. ORNSTEIN in formula (I) of his paper. He finds

$$C = -\frac{\left(\frac{dt}{dp}\right)_0 \left[k_2 \frac{k_1 - {}^d/_R (k_1 - k_2)}{k_2 + {}^d/_R (k_1 - k_2)} + k_3\right]}{\pi R^2 W S_i} \quad . \quad . \quad . \quad (2)$$

Here k_1, k_2 and k_3 are the coefficients of heat conductivity respectively of the wire, of water and the ice, $\left(\frac{dt}{dp}\right)_0$ is the rise of the melting temperature by pressure, measured at the melting temperature, W is the latent heat of melting ice, S_i the specific gravity of ice, R the radius of the wire and d the thickness of the layer of water. Now the value of C cannot be calculated by this formula, since the quantity d is unknown. But besides the equation (I) Mr. ORNSTEIN gives in his formula (II^c) an expression, found by a hydrodynamical reasoning, in which the quantity d likewise occurs. This relation is [1]):

$$v = \frac{S_w}{S_i} \frac{2\alpha P}{12 \pi \mu d_1 \sin \alpha} \left(\frac{d}{R}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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1) In Mr. ORNSTEIN's paper this formula is given without the factor $\frac{S_w}{S_i}$ since this latter has no perceptible influence.

Here S_w is the specific gravity of water at 0°, μ the viscosity coefficient. By equalising (1) and (3) we find:

$$C = \frac{S_w}{S_i} \cdot \frac{1}{12\,\pi\,\mu} \left(\frac{d}{R}\right)^3 \quad \ldots\ldots\ldots \quad (4)$$

and we should now have to eliminate $\frac{d}{R}$ between (2) and (4). In order to perform this elimination we simplify (2). We consider the form in (2) between the brackets [ ] and keep in mind that $\frac{d}{R}$ is very small, that k_1 is very much greater than k_2 and that k_3 may be neglected with respect to the first term (which amounts to neglecting the conduction of heat through the ice).

We may then write:

$$k_2 \frac{k_1 - {}^d/_R (k_1 - k_2)}{k_2 + {}^d/_R (k_1 - k_2)} = k_2 \frac{k_1}{k_2 + {}^d/_R k_1} = \frac{k_1}{1 + {}^d/_R \frac{k_1}{k_2}}.$$

Then we have

$$C = - \frac{\left(\frac{dt}{dp}\right)_0 \frac{k_1}{1 + {}^d/_R \frac{k_1}{k_2}}}{\pi R^2 W S_i}$$

If we put

$$\left(\frac{dt}{dp}\right)_0 = - 7.4 \times 10^{-8},\ S_i = 0.9167,\ W = 79.2,$$

C becomes

$$C = 3.3 \times 10^{-11} \times \frac{1}{R^2} \frac{k_1}{1 + {}^d/_R \frac{k_1}{k_2}}.$$

In (4) we substitute

$$S_w = 1,\ S_i = 0.9167,\ \mu = 0.0181,$$

then

$$C = 1.600 \left(\frac{d}{R}\right)^3 \quad \ldots\ldots\ldots \quad (5)$$

Equalising the two values of C we have:

$$\left(\frac{d}{R}\right)^3 = 2.0 \times 10^{-11} \frac{1}{R^2} \frac{k_1}{1 + \frac{d}{R} \frac{k_1}{k_2}}$$

or

$$\left(\frac{d}{R}\right)^3 + \left(\frac{d}{R}\right)^4 \frac{k_1}{k_2} = 2.0 \times 10^{-11} \frac{k_1}{R^2}.$$

From this equation $\frac{d}{R}$ can easily be found by a tentative method, when k_1, k_2 and R are given. In the different cases we find (in CGS-units),

Steel wire	$k_1 = 0.166$	$k_2 = 0.0015$	$R = 0.025$	$\frac{d}{R} = 0.00166$
	$k_1 = 0.166$	$k_2 = 0.0015$	$R = 0.020$	$\frac{d}{R} = 0.00190$
	$k_1 = 0.166$	$k_2 = 0.0015$	$R = 0.015$	$\frac{d}{R} = 0.00229$
German silver wire	$k_1 = 0\ 070$	$k_2 = 0.0015$	$R = 0.025$	$\frac{d}{R} = 0.00128$
	$k_1 = 0.070$	$k_2 = 0.0015$	$R = 0.020$	$\frac{d}{R} = 0.00149$
	$k_1 = 0.070$	$k_2 = 0.0015$	$R = 0.015$	$\frac{d}{R} = 0.00179$
Silver wire	$k_1 = 1.50$	$k_2 = 0.0015$	$R = 0.025$	$\frac{d}{R} = 0.00239$
	$k_1 = 1.50$	$k_2 = 0.0015$	$R = 0.020$	$\frac{d}{R} = 0.00279$
	$k_1 = 1\ 50$	$k_2 = 0.0015$	$R = 0.015$	$\frac{d}{R} = 0.00318$

C is then found by substitution in (5). These values are given below, together with the values found by experiment, but now expressed in CGS-units.

		Calculated	*Found*
Steel wire	$R = 0.025$	73×10^{-10}	29×10^{-10}
	$R = 0.020$	110×10^{-10}	49×10^{-10}
	$R = 0.015$	192×10^{-10}	72×10^{-10}
German silver wire	$R = 0.025$	34×10^{-10}	24×10^{-10}
	$R = 0{,}020$	53×10^{-10}	37×10^{-10}
	$R = 0.015$	91×10^{-10}	59×10^{-10}
Silver wire	$R = 0.025$	218×10^{-10}	46×10^{-10}
	$R = 0.020$	347×10^{-10}	66×10^{-10}
	$R = 0.015$	519×10^{-10}	70×10^{-10}

The agreement must be called bad for the silver wire, satisfactory for the german silver wire. It may be called satisfactory, since different circumstances may be mentioned which make us expect a too small value. Leaving aside the great uncertainty in the values of the heat conductivities of metals, to which we cannot here ascribe the bad agreement, since we do not know in which direction this

will influence the result[1]), the following causes may be mentioned.

1. The roughness of the wires. Already Mr. ORNSTEIN pointed this out. If the wire is not entirely smooth, the hydrodynamical deductions are uncertain and hence also formula (3). In order to ascertain the influence of this roughness I made some experiments with a steel wire that had for a moment been scoured with fine sand-paper in the direction of its length. Macroscopically no result of this manipulation could be discovered on the wire. Yet the effect proved considerable, for the following results were found:

	P	C	
steel wire, diameter 0,5 m.M.	455	0,009	average 0.011 m.M.
	1255	0,011	
	2205	0,014	
steel wire, diameter 0,3 m.M.	1255	0,028	

So we find a diminution of about 40 % in the value of C. After having observed this influence I tried to obtain smooth wires, but unsuccessfully; all the wires that were used in the experiments showed under the microscope numberless grooves in the direction of their length and of a breadth that might be estimated at somewhat less than 0.01 mm.

Since it is easily deduced from the calculated values of $\frac{d}{R}$ that the thickness of the layer of water increases with the size of the radius of the wire and since the influence of the roughness of the wire will be smaller with a greater thickness of this layer of water, I have still made some measurements with a thicker steel wire of 0,87 mm. diameter and heavier weights. The result was:

P	C		C (in C.G.S. units)
25200	0,00803	0,0081	13.8×10^{-10}
25200	0,00822		
5200	0,00667		11.3×10^{-10}

while calculation gives

$$k_1 = 0{,}166, \quad k_2 = 0{,}0015, \quad R = 0{,}0435 \quad \frac{d}{R} = 0{,}00120 \quad C = 27.7 \times 10^{-10}$$

The agreement is now better indeed; the value found is half the calculated one, while with the thinner steel wires it was slightly more than a third.

[1]) The values given by F. KOHLRAUSCH (Lehrbuch der praktischen Physik 10 Auflage 1905), steel $k = 0.06$ to 0.12 and silver $k = 1.01$, would give a much better agreement.

2. In the deduction of formula (1) it was assumed that within the layer of water the relation

$$\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}=0.$$

holds. This relation, however, holds for a body at rest. Here, on the other hand, we have to deal with a streaming liquid, in which case the following formula holds:

$$\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}=\frac{\varrho S_w}{k_z}\left(u\frac{\partial t}{\partial x}+v\frac{\partial t}{\partial y}\right).$$

Here ϱ is the specific heat of the liquid, u and v the velocity components in the X- and Y-directions. If we use this formula we take into account that the heat, conducted through the wire, does not entirely serve for melting the ice, but that it is partly conveyed upwards again by the streaming liquid. This also must result in a diminution of the velocity of descent. Prof. LORENTZ informed me, however, that it can be shown that this influence must be regarded as a quantity of the second order, so that the differences cannot be explained in this way.

3. If the temperature in the interior of the block of ice is not exactly 0°, but lower, the velocity of descent will also become smaller. But I observed no phenomena which point to a lower temperature in the interior. Blocks of ice that had been kept for 24 hours in a space above 0° gave the same results as blocks that had just been received. Moreover the wires as a rule went down at a distance of only a few millimetres from one of the faces of the block, and in some experiments they even came out of the block by melting of that face. Yet in the last moment, before the wire came out, no acceleration of the descent was observed.

Nor does theory support such an explanation. Prof. LORENTZ informed me that when the surface of a ball of ice of 3 centimeters diameter and at a temperature of $-2°$, is raised to 0° and kept at this temperature, it may be shown that in less than an hour the temperature at the centre has risen to $-0.01°$.

4. Another important influence on the velocity of descent is found in the fact that it is possible that not all the ice, melting at the lower side of the wire, freezes again exactly at the upper side, but that this water perhaps flows off laterally. It is clear that this must have a great influence since then the heat, necessary for the melting, is furnished by conduction through the ice. Already J. THOMSON

BOTTOMLEY [1]) showed that the lateral flow of water causes a great retardation.

The experiments now showed that this lateral flow really exists. For even when the ice was perfectly clear, in the places where the wire had passed through it various small bubbles were observed. Consequently not all the ice had been re-formed which had been there.

In this respect I also mention a curious change, found in the values of C: these values rise with the weight. This is very conspicuous with the silver and german silver wires, but also with the steel wires it exists, especially with the thick one of 0.87 mm.

Accordingly it was often seen that the bubbles on the path of the wire were more numerous with small than with heavy weights. This became particularly clear in experiments in which, during one descent, first a heavy and then a small weight was used. With the smaller weight more water flows off laterally.

I still made several experiments in which the wire was pulled upwards through the ice, hoping to prevent this lateral flow. The result was not the expected one, for bubbles also appeared and the values, found for C, were even somewhat smaller than in the former case. In regard to this question it would be desirable to investigate the descent of a whole body, e.g. of an iron ball, through perfectly clear ice.

In my opinion this lateral flow is the chief reason why theory and observation disagree. It also explains why with the silver wires larger differences were found than with the german silver and the steel wires. For if the heat is only partly furnished by the freezing process above the wire and if the rest has to be furnished by conduction through the ice, it seems to be of little consequence whether the wire be a good conductor of heat.

5. Ice is a crystalline substance. This also may have its effect. Perhaps the melting point is not the same at the different faces of the crystals which the wire touches. Though this influence may exist, we cannot say in which direction it would modify the result.

In order to find out whether such an influence makes itself felt, I made the wire pass several times through the same block of ice in three mutually perpendicular directions. But no perceptible difference was found.

As the general result of the experiments I think we may state, that they indicate that the regelation theory will be found capable of explaining the phenomena not only qualitatively but also quantitatively.

[1]) Pogg. Ann. 148, p. 492, 1871.

Physics. — *"Contribution to the theory of binary mixtures, II"*, by Prof. J. D. VAN DER WAALS. (Continued, see p. 621).

Not to suspend too long the description of the course of the q-lines in the case that the locus $\frac{d^2\psi}{dx^2} = 0$ exists, we shall postpone the determination of the temperature at which this locus has disappeared, and the inquiry into the value of x and v for the point at which it disappears — and proceed to indicate the modification in the course of the q-lines which is the consequence of its existence.

From the value of $\frac{dv}{dx_q} = -\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$ follows that when a q-line passes through the curve $\frac{d^2\psi}{dx^2} = 0$, it has a direction parallel to the

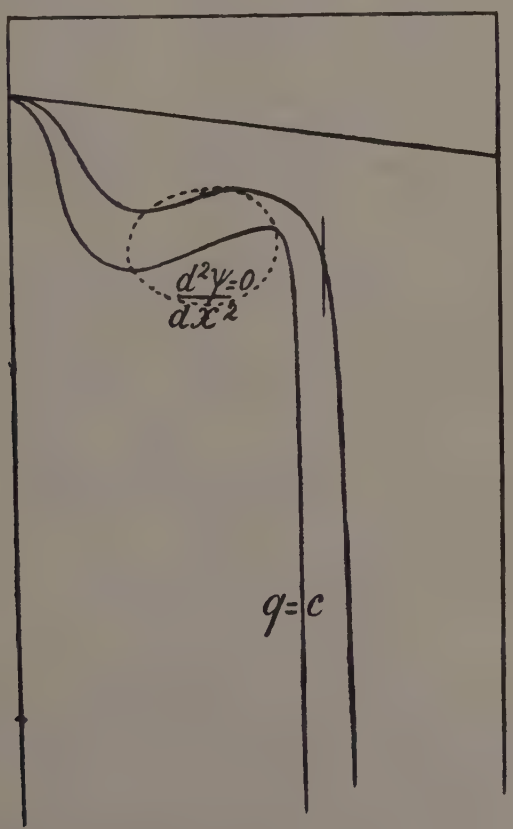

Fig. 3.

x-axis in such a point of intersection. So a q-line meeting $\frac{d^2\psi}{dx^2} = 0$, will be twice directed parallel to the x-axis, and have a shape as represented in fig. 3 — at least as long as the curve $\frac{d^2\psi}{dxdv} = \left(\frac{dp}{dx}\right)_v = 0$ does not occur. Such a shape may, therefore, be found for the q-lines, in the case that the second component has a higher value of b, and lower value of T_k —, and such a shape will certainly present itself in the case mentioned when the temperature is low enough.

Then there is a group of q-lines, for which maximum volume, and minimum volume is found. The outmost line on one side of this group of q-lines, viz. that for which q possesses the highest value, is that for which maximum and minimum volume have coincided, and which touches the curve $\frac{d^2\psi}{dx^2} = 0$ in the point, in which this curve itself has the smallest volume. The other outmost line of this group of q-lines, viz. that for which q possesses the smallest value, is that for which again maximum and minimum volume have coincided, and which also touches the curve $\frac{d^2\psi}{dx^2} = 0$, but in that point in which this curve itself has its largest volume. So for these two points of contact the equation $\frac{d^3\psi}{dx^3} = 0$ holds. These two points of contact are, therefore, found by examining where the curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^3\psi}{dx^3} = 0$ intersect. This last locus appears to be independent of the temperature, as we may put $\frac{d^3a}{dx^3}$ equal to 0. We find from the equation on p. 638

$$\frac{d^3\psi}{dx^3} = MRT \left\{ -\frac{1-2x}{x^2(1-x)^2} + 2\frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3} + \frac{\frac{d^2b}{dx^2}}{(v-b)^2} \right\} = 0.$$

If we neglect $\frac{d^2b}{dx^2}$, we find from $\frac{d^3\psi}{dx^3} = 0$

$$\frac{\frac{db}{dx}}{v-b} = \sqrt[3]{\frac{1-2x}{2x^2(1-x)^2}}.$$

The locus $\frac{d^3\psi}{dx^3} = 0$ occurs, therefore, only in the left side of the figure or for values of x below $\frac{1}{2}$. The line $x = {}^1/_2$ is an asymptote for this curve, and only at infinite volume this value of x is reached.

And as for $x = 0$ also $r - b$ must be $= 0$, the curve $\frac{d^3\psi}{dx^3} = 0$ starts from the same point from which all the q-lines start. If $\frac{d^2b}{dx^2}$ should not be equal to 0, we have ground for putting this quantity positive (Cont. II, p. 21), and we arrive at the same result for the initial point and the final point of the curve $\frac{d^3\psi}{dx^3} = 0$.

So the points of the curve $\frac{d^2\psi}{dx^2} = 0$, where tangents may be drawn to it parallel to the x-axis, lie certainly at values of x smaller than $\frac{1}{2}$, and accordingly the two outer ones of the group of the q-lines with maximum and minimum volume have their horizontal tangents also in the left side of the figure. The q-line with the highest value of q at lower value of x than that with the lowest value. This is represented in fig. 4.

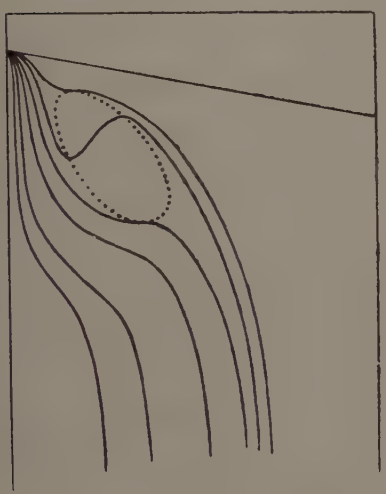

Fig. 4.

We notice at the same time that the points in which a q-line touches the curve $\frac{d^2\psi}{dx^2} = 0$, are points of inflection for such a q-line, just as this is the case with the p-lines when a p-line touches the curve $\frac{d^2\psi}{dv^2}$. From

$$q = \left(\frac{d\psi}{dx}\right)_v$$

follows:

$$\frac{d^2\psi}{dxdv}\left(\frac{dv}{dx}\right)_q + \frac{d^2\psi}{dx^2} = 0,$$

and

$$\frac{d^2\psi}{dxdv}\frac{d^2v}{dx^2}_q + \left\{\frac{d^3\psi}{dxdv^2}\left(\frac{dv}{dx}\right)^2_q + 2\frac{d^3\psi}{dx^2dv}\left(\frac{dv}{dx}\right)_q + \frac{d^3\psi}{dx^3}\right\} = 0.$$

In the points mentioned $\left(\frac{dv}{dx}\right)_q = 0$, because $\frac{d^2\psi}{dx^2} = 0$, and at the

same time $\frac{d^3\psi}{dx^3} = 0$. Hence $\left(\frac{d^2v}{dx^2}\right)_q = 0$, which appears also immediately from the figure.

Within the curve $\frac{d^2\psi}{dx^2} = 0$ every q-line that intersects it, has also a point of inflection, because the latter must pass from minimum volume to maximum volume in its course. So there is a continuous series of points in which q-lines possess points of inflection between the two points in which horizontal tangents may be drawn to $\frac{d^2\psi}{dx^2} = 0$. But there is also a continuous series of points in which the q-lines must possess points of inflection on the left of the curve $\frac{d^2\psi}{dx^2} = 0$, so with smaller value of x. For every q-line has its convex side turned to the x-axis just after it has left the starting point. If it is to enter the curve $\frac{d^2\psi}{dx^2} = 0$ in horizontal direction and to pass then to smaller volume, it must turn its concave side to the x-axis in that point, and so it must have previously possessed a point of inflection. Most probably the last-mentioned branch is somewhere continuously joined to the first mentioned one. If so, there is a closed curve in which $\frac{d^2v}{dx^2}_q = 0$ — and then it may be expected that this closed curve contracts with rise of T, and has disappeared above a certain temperature. But these and other particulars may be left to a later investigation.

We have now described the shape of the q-lines, 1. in the case that neither $\frac{d^2\psi}{dx^2}$, nor $\frac{d^2\psi}{dxdv}$ is equal to 0, 2. in the case that the curve $\frac{d^2\psi}{dxdv} = 0$ exists, 3. in the case that the curve $\frac{d^2\psi}{dx^2} = 0$ is found. It remains to examine the course of the q-lines when both curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dxdv} = 0$ exist.

For the occurrence of the $\frac{d^2\psi}{dx^2} = 0$ it is only required that $\frac{d^2a}{dx^2}$ be positive, as we shall always suppose, and that T is below the value of the temperature at which the curve $\frac{d^2\psi}{dx^2} = 0$ has contracted to a single point. It may, therefore, occur with every binary system, without our having to pay attention to the choice of the components.

But the occurrence of the curve $\frac{d^2\psi}{dxdv} = \left(\frac{dp}{dx}\right)_v = 0$ is not always possible, as we already showed in the discussion of the shape of the isobars. If we consult fig. 1 (These Proc. IX p. 630) it appears that the curve $\left(\frac{dp}{dx}\right)_v = 0$ does not exist throughout the whole width of the diagram of isobars.

With mixtures for which the course of the isobars is, as is the case in the left side of the figure, the line $\left(\frac{dp}{dx}\right)_v = 0$ does not exist at all. Only with mixtures for which the course of the isobars is represented by the middle part of fig. 1 it exists and if the asymptote is found, it can occur with all kinds of volumes. Also with mixtures for which the course of the isobars is represented by the right part of fig. 1, it exists, but then only at very small volumes, and it possesses only the branch which approaches the line $v = b$ asymptotically.

Let us now consider a mixture such that the curve $\left(\frac{dp}{dx}\right)_v = 0$ is really present at such a temperature that also the curve $\frac{d^2\psi}{dx^2} = 0$ exists; then we have still to distinguish between two cases, i. e. 1. when the two loci mentioned do not intersect, and 2. when they do intersect. If they do not intersect, and the curve $\left(\frac{dp}{dx}\right)_v = 0$ lies on the right of $\frac{d^2\psi}{dx^2} = 0$, then the q-line, after having had its maximum and minimum volume, will intersect the line $\left(\frac{dp}{dx}\right)_v = 0$, in that point of intersection will have a tangent // v-axis; it will further run back to smaller volume, just as this is the case with one of the q-lines drawn in fig. 2. This may e.g. occur for mixtures corresponding to the left region of the diagram of isobars, when this region is so wide that also the asymptote and a further part of the curve $\left(\frac{dp}{dx}\right)_v = 0$ is found. If with non-intersection the relative position of the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\left(\frac{dp}{dx}\right)_v = 0$ are reversed, this can probably not occur but for mixtures which correspond to a region of the diagram of isobars which has been chosen far on the right side. The course of the q-lines which then pass through the curve $\frac{d^2\psi}{dx^2} = 0$, is represented in fig. 5. But when the two

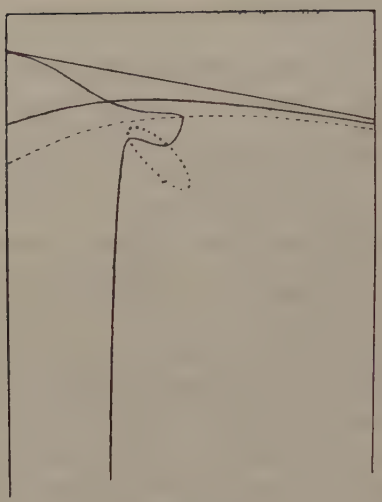

Fig. 5.

curves $\frac{d^2\psi}{dx^2}=0$ and $\left(\frac{dp}{dx}\right)_v=0$ intersect, which then necessarily takes place in 2 points, the shape of the q-lines is much more intricate. Then numerator and denominator are equal to zero in

$$\left(\frac{dv}{dx}\right)_q=\frac{\frac{d^2\psi}{dx^2}}{\left(\frac{dp}{dx}\right)_v},$$

and $\left(\frac{dv}{dx}\right)_q$ is not to be determined from this equation. Then $\left(\frac{dv}{dx}\right)_q$ must be determined from :

$$\left(\frac{d^3\psi}{dxdv^2}\right)\left(\frac{dv}{dx}\right)_q^2+2\left(\frac{d^3\psi}{dx^2dv}\right)\left(\frac{dv}{dx}\right)_q+\left(\frac{d^3\psi}{dx^3}\right)=0.$$

In the discussion of the shape of the p-lines we came across an analogous case when the curves $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dxdv}=0$ intersect; and there we found that the two points of intersection had a different character. For one point of intersection the p-line has two different real directions, depending on the sign of $\frac{d^3\psi}{dv^3}\frac{d^3\psi}{dvdx^2}-\left(\frac{d^3\psi}{dxdv^2}\right)^2$. If this expression was negative, the loop-isobar passed through that point of intersection. In the same way, when from the above quadratic equation for $\left(\frac{dv}{dx}\right)_q$ we write the condition on which the roots are real, we find the condition :

$$\left[\frac{d^3\psi}{dx^3}\frac{d^3\psi}{dxdv^2}-\left(\frac{d^3\psi}{dx^2dv}\right)^2\right]\text{negative;}$$

which may be immediately found from the condition for the loop of the *loop-isobar*, as requirement for the loop of the *loop-q-line*, when we interchange x and v.

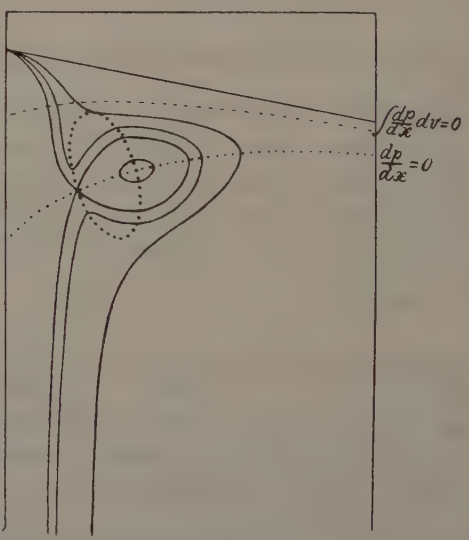

Fig. 6.

The q-line which passes through the first point where the above condition is negative, has, therefore, a real double point, and runs round the other point of intersection before passing through this double point for the second time. In Fig. 6 the dotted closed curve $\frac{d^3\psi}{dx^2} = 0$ has been traced, and also the dotted curve $\left(\frac{dp}{dx}\right) = -\left(\frac{d^2\psi}{dvdx}\right) = 0$. The point of intersection lying on the left, is the double point. According to what was stated before, $\frac{d^3\psi}{dx^3}$ is negative in this point, and the quantity $\frac{d^3\psi}{dxdv^2}$ is positive, which is also to be deduced from what was mentioned previously about the sign of $\frac{d^2p}{dxdv} = -\frac{d^3\psi}{dxdv^2}$. So the criterion by which the reality of the two directions of $\left(\frac{dv}{dx}\right)_q$ is tested is satisfied in that point of intersection. In the second point of intersection $\frac{d^3\psi}{dx^3}$ is positive, and $\frac{d^3\psi}{dxdv^2}$ is also positive. It is true that it does not follow from this that $\frac{d^3\psi}{dx^2}\frac{d^3\psi}{dxdv^2} > \left(\frac{d^3\psi}{dvdx^2}\right)^2$ — but 1 it appears in the drawing of the loop-q-line that there is no other possibility but that it runs round the second point of intersection, and 2 it appears, that just as we have mentioned in the analogous case for the shape of the p-lines (Footnote p. 626), only when the two points of intersection coincide, so when the two curves $\frac{d^3\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dxdv} = 0$ touch, the quantity $\frac{d^3\psi}{dx^3}\frac{d^3\psi}{dxdv^2} - \left(\frac{d^3\psi}{dvdx^2}\right)^2$ is equal to 0. In the case that $\frac{d^2\psi}{dx^2} = 0$ has greater dimensions, so at lower temperature, the loop-q-line will, of course, extend still much more to the right, and the higher q-lines must be strongly compressed at the point where the curve $\left(\frac{dp}{dx}\right)_v = 0$ cuts the second axis (the line $x = 1$).

This loop-q-line determines the course of all the other q-lines. Thus in fig. 6 a somewhat higher q-line passes through $\frac{d^2\psi}{dx^2} = 0$, in vertical direction just above the double point, rises then till it

passes through this curve for the second time, reaches its highest point, after which it meets the curve $\left(\frac{dp}{dx}\right)_v = 0$ in vertical direction, and then pursues its course downward after having been directed horizontally twice more.

It must then again approach asymptotically that value of x, at which it intersected the line $\int \frac{dp}{dx}\, dv = 0$ shortly after the beginning of its course. This line has also been drawn in fig. 6. It is evident that it may not intersect the curve $\frac{d^2\psi}{dx^2} = 0$. In fig. 6 it has, accordingly, remained restricted to smaller volumes than those of the curve $\frac{d^2\psi}{dx^2} = 0$. For the assumption of intersection involves that a q-line could meet the locus $\int \frac{dp}{dx}\, dv = 0$ several times. As $q = MRT\, l\frac{x}{1-x}$ in such a meeting point, it follows from this that only one value of x can belong to given q. It deserves notice that in this way without any calculation we can state this thesis: "The curves $\frac{d^2\psi}{dx^2} = 0$ and $\int \frac{dp}{dx}\, dv = 0$ can never intersect." According to the equation of state it would run like this: "The equations:

$$MRT\left\{\frac{1}{x\,(1-x)} + \frac{\left(\frac{db}{dx}\right)^2}{(v-b)^2}\right\} = \frac{\frac{d^2a}{dx^2}}{v} \text{ and } \frac{MRT\,\frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{v}$$

can have no solution in common. Indeed, if v from the second equation is expressed in x and T, and if this value is substituted in the first equation, we get the following quadratic equation in MRT:

$$(MRT)^2\left\{\frac{1}{x\,(1-x)} + \frac{1}{b^2}\left(\frac{db}{dx}\right)^2 + \frac{1}{b}\,\frac{db}{dx}\,\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}\right\} -$$

$$- 2\,(MRT)\left\{\frac{1}{b^2}\,\frac{db}{dx}\,\frac{da}{dx} - \frac{1}{b}\,\frac{1}{2}\,\frac{d^2a}{dx^2}\right\} + \frac{1}{b^2}\left(\frac{da}{da}\right)^2 = 0.$$

A value of MRT, which must necessarily be positive to have

significance, requires $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} > \frac{1}{2b}\frac{d^2a}{dx^2}$. From the foregoing remarks it is sufficiently clear that $\frac{da}{dx}$ must be positive to render the locus $\int\frac{dp}{dx}\,dv = 0$ possible, and that $\frac{d^2a}{dx^2}$ must be positive to render $\frac{d^2\psi}{dx^2} = 0$ possible. The roots of the given quadratic equation, however, are then imaginary, the square of $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx} - \frac{1}{2b}\frac{d^2a}{dx^2}$ being necessarily smaller than the square of $\frac{1}{b^2}\frac{db}{dx}\frac{da}{dx}$, and the square of this being smaller than the product of $\frac{1}{b^2}\left(\frac{da}{dx}\right)^2$ and the factor of (MRT).

But let us return to the description of the course of the remaining q-lines. There is, of course, a highest q-line, which only touches the locus $\frac{d^2\psi}{dx^2} = 0$, directed horizontally in that point of contact, and for which also $\frac{d^3\psi}{dx^3} = 0$ in that point. There is also a q-line which touches the locus $\frac{d^2\psi}{dx^2} = 0$ in its downmost point, and which as a rule will be another than that which touches it in its highest point. The q-lines of higher degree than the higher of these two have again the simple course which we have traced in fig. 2 (p. 635) for that q-line which intersects the locus $\left(\frac{dp}{dx}\right)_v = 0$. Only through their considerable widening all of them will more or less evince the influence of the existence of the above described complication. The q-lines of lower degree than the loop-q-line have split up into two parts, one part lying on the left which shows the normal course of a q-line which cuts $\left(\frac{dp}{dv}\right)_v = 0$; and a detached closed part which remains enclosed within the loop. Such a closed part runs round the second point of intersection which $\left(\frac{dp}{dx}\right)_v = 0$ and $\frac{d^2\psi}{dx^2} = 0$ have in common, passes in its lowest and highest point through $\frac{d^2\psi}{dx^2} = 0$, and through $\left(\frac{dp}{dx}\right)_v = 0$ in the point lying most to the right and most to the left. With continued decrease of the degree of q this detached

part contracts, and disappears as isolated point. This takes place before q has descended to negative infinite, so that q-lines of very low degree have entirely resumed the simple course which such lines have when only the curve $\left(\frac{dp}{dx}\right)_v = 0$ exists.

Also in this general case for the course of the q-lines we can form an opinion about the locus of the points of inflection of these curves, so of the points in which $\left(\frac{d^2v}{dx^2}\right)_q = 0$. We already mentioned above that when the line $\left(\frac{dp}{dx}\right)_v = 0$ exists at a certain distance from it there must be points of inflection on the q-lines at larger volume. If also the asymptote of $\left(\frac{dp}{dx}\right)_v = 0$ should exist, also this series of points of inflection of the q-lines has evidently the same asymptote. In fig. 6 this asymptote lies outside the figure, and so it is not represented — but the remaining part is represented, modified, however, in its shape by the existence of the double point. The said series of points of inflection is now sooner to be considered as consisting of two series which meet in the double point, and which have, therefore, got into the immediate neighbourhood of the line $\left(\frac{dp}{dx}\right)_v = 0$ there. So there comes a series from the left, which as it approaches the double point, draws nearer to $\left(\frac{dp}{dx}\right)_v = 0$, and from the double point there goes a series to the right, which first remains within the space in which $\frac{d^2\psi}{dx^2} = 0$ is found, and which passes through the lowest point of this curve, but then moves further to the side of the second component at larger volume than that of the curve $\left(\frac{dp}{dx}\right)_v = 0$. The double point of the q-loop-line is, therefore, also double point for the locus of the points of inflection of the q-lines, and the continuation of the two branches which we mentioned above, must be found above the curve $\left(\frac{dp}{dx}\right)_v = 0$. Accordingly, we have there a right branch, which runs within $\frac{d^2\psi}{dx^2} = 0$, and passes through the highest point of this curve, and a left branch which from the double point runs to the left of the loop-q-line, and probably merges into the preceding

branch. If this is the case the outmost q-lines on the two sides, both that lying very low and that lying very high, have no points of inflection.

THE SPINODAL CURVE AND THE PLAITPOINTS.

The spinodal curve is the locus of the points in which a p- and a q-line meet. In these points $\frac{dv}{dx_p} = \frac{dv}{dx_q}$ and so $-\frac{\frac{d^2\psi}{dxdv}}{\frac{d^2\psi}{dv^2}} = -\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$ or $\frac{d^2\psi}{dv^2}\frac{d^2\psi}{dx^2} = \left(\frac{d^2\psi}{dxdx}\right)^2$. In order to judge about the existence of such points of contact, we shall have to trace the p and the q lines together. As appears from fig. 1 p. 630 the shape of the p-lines is very different according as a region is chosen lying on the left side, or in the middle or on the right side; but the course of the q-lines in the different regions is in so far independent of the choice of the regions that $q_{-\infty}$ always represents the series of the possible volumes of the first component, and $q_{+\infty}$ the series of the possible volumes of the second component, and also the line of the limiting volumes. As the shape of the p-lines can be so very different we shall not be able to represent the shape of the spinodal line by a single figure. Besides the course of the p-lines depends on the existence or non-existence of the curve $-\frac{dp}{dv} = \frac{d^2\psi}{dv^2} = 0$, and the course of the q-lines on the existence or non-existence of the curve $\frac{d^2\psi}{dx^2} = 0$, and besides, and this holds for both, on the existence of the curve $\frac{d^2\psi}{dxdv} = 0$. Hence if for all possible cases we would illustrate the course of the spinodal curve in details by figures, this examination would become too lengthy. We shall, therefore, have to restrict ourselves, and try to discuss at least the main points.

Let us for this purpose choose in the first place a region from the left side of the general p-figure, and let us think the temperature so low, so below $(T_k)_1$, that there are still two isolated branches for the curve $\frac{dp}{dv} = 0$ all over the width of the region.

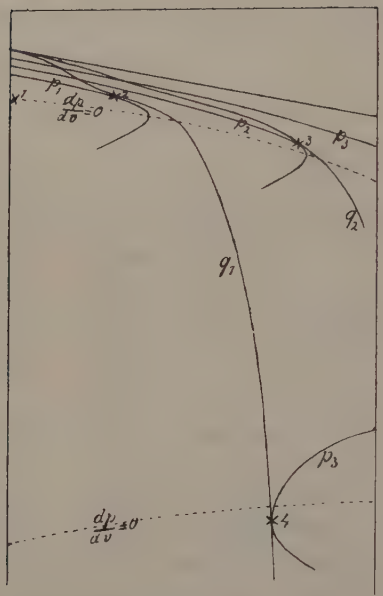

Fig. 7.

In fig. 7 T is thought higher than the temperature at which $\frac{d^2\psi}{dx^2}=0$ vanishes, and in fig. 8 below this temperature. In fig. 7 all the q-lines have the very simple course which we previously indicated for them, and the p-lines the well-known course, with which $\left(\frac{dv}{dx}\right)_p$ is positive on the liquid side of $\frac{dp}{dv}=0$, and on the vapour side of $\frac{dp}{dv}=0$, negative between the two branches of this curve, the transition of $\left(\frac{dv}{dx}\right)_p$ from positive to negative taking place through infinitely large. The isobars p_1, p_2 and p_3 have been indicated in the figure, in which $p_1<p_2<p_3$. Also a few q-lines, $q_1<q_2$ and the points of contact of p_1 to q_1 and of p_3 to q_2. Also on the vapour side a point of contact of p_3 to q_1. It is clear 1st that every q-line yields two points for the spinodal curve, and 2nd that these points of contact lie outside the region in which $\frac{dp}{dv}$ is positive. On the other hand we see that the distance from the spinodal curve to the curve $\frac{dp}{dv}=0$ can be nowhere very large. Only by drawing very accurately it can be made evident that on the vapour side the spinodal curve has always a somewhat larger volume than the vapour branch of the curve $\frac{dp}{dv}=0$. In the four points, in which $\frac{dp}{dv}=0$ intersects the sides, indeed, the spinodal line coincides with this curve.

Fig. 7*b* has been drawn to give an insight into the circumstances at the plaitpoint. At $T>(T_k)_2$ the two branches of the curve $\frac{dp}{dv}=0$ have united at that value of x, for which $T=(T_k)_2$. One of the p-lines, namely that of the value $p=(p_k)_x$, touches in the

point at which the two branches have joined at a volume $v = (v_k)_x$, and has a point of inflection there. Two parts of q-lines have been drawn as touching the p-line. The two points of contact (1) and (2) are points of the spinodal curve, and lie again outside the curve $\frac{dp}{dv} = 0$. For a higher p-line these points will come closer together. And the place where they coincide is the plaitpoint. As in point (1) $\left(\frac{d^2v}{dx^2}\right)_p > \left(\frac{d^2v}{dx^2}\right)_q$ and reversely in point(2) $\left(\frac{d^2v}{dx^2}\right)_q > \left(\frac{d^2v}{dx^2}\right)_p$, $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$ when (1) and (2) have coincided, and this may be considered as the criterion for the plaitpoint so that in such a point the two equations:

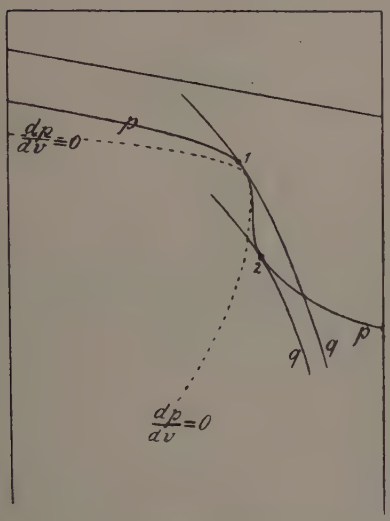

Fig. 7b.

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$$

and

$$\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$$

hold.

The following remark may not be superfluous. In point (2) $\left(\frac{d^2v}{dx^2}\right)_p$ is not only smaller than $\left(\frac{d^2v}{dx^2}\right)_q$, but even negative. In order to find the plaitpoint, the point in which 2 points of contact for the q and the p-lines coincide, and so $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have the same value, $\left(\frac{d^2v}{dx^2}\right)_p$ must first reverse its sign in the point (2) with increase of the value of p for the isobar before the equality with $\left(\frac{d^2v}{dx^2}\right)_q$ can be obtained. And that, at least in this case, this reversal of sign must take place with point (2) and not with point (1), appears from the positive value of $\left(\frac{d^2v}{dx^2}\right)_q$. So we arrive here at the already known theses that in the plaitpoint the isobar surrounds the spinodal curve, and also the binodal one.

As

$$dv_p = \left(\frac{dv}{dx}\right)_p dx + \frac{1}{1.2}\left(\frac{d^2v}{dx^2}\right)_p dx^2 + \frac{1}{1.2.3}\left(\frac{d^3v}{dx^3}\right)_p dx^3 \text{ etc.}$$

and

$$dv_q = \left(\frac{dv}{dx}\right)_q dx + \frac{1}{1.2}\left(\frac{d^2v}{dx^2}\right)_q dx^2 + \frac{1}{1.2.3}\left(\frac{d^3v}{dx^3}\right)_q dx^3 \text{ etc.}$$

we find for a plaitpoint:

$$dv_p - dv_q = \frac{1}{1.2.3}\left\{\left(\frac{d^3v}{dx^3}\right)_p - \left(\frac{d^3v}{dx^3}\right)_q\right\} dx^3 \text{ etc.}$$

So the p- and the q-lines meet and intersect in a plaitpoint, and this is not always changed when a point should be a double plaitpoint. We shall, namely, see later on that the criterion for a double plaitpoint is sometimes as follows:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$$

and

$$\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q = 0.$$

Let us now proceed to the discussion of the case represented by fig. 8. Here it is assumed that T lies below the temperature at which $\frac{d^2\psi}{dx^2} = 0$ vanishes, so that this locus exists, it being moreover supposed that it intersects the curve $\frac{dp}{dv} = 0$. It appears from the drawing that for the q-lines for which maximum and minimum volume occurs, two new points of contact with the p-lines are necessarily found in the neighbourhood of the points of largest and smallest volumes at least for so far as these points lie on the liquid side of $\frac{dp}{dv} = 0$.

So there is a group of q-lines on which 4 points of the spinodal curve occur, and which will therefore intersect the spinodal curve in 4 points. The two new points of contact lie on either side of $\frac{d^2\psi}{dx^2} = 0$, and these two new points of contact do not move far away from this curve, the two old points of contact not being far removed from $\frac{dp}{dv} = 0$.

If we raise the value of q, the two new points of contact draw nearer to each other. Thus e. g. the q-line which touches $\frac{d^2\psi}{dx^2}$ in its highest point, and for which $\left(\frac{dv}{dx}\right)_q = 0$ and also $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in that

point has also been drawn in the figure. Also this q-line may still be touched by two different p-lines, which, however, have not been represented in the drawing. For a still higher q-line these points would coincide, and in consequence of the coincidence of two points of the spinodal curve a plaitpoint would then be formed. $\left(\frac{d^2v}{dx^2}\right)_v$ always being positive, $\left(\frac{d^2v}{dx^2}\right)_q$, which has been negative for a long time in the point lying on the left side, must first reverse its sign before it can coincide with the point lying on the right — a remark analogous to that which we made for the plaitpoint that we discussed above.

If on the other hand the value of q is made to descend, the point of contact lying most to the left will move further and further from the curve $\frac{d^2\psi}{dx^2} = 0$, and nearer and nearer to the curve $\frac{dp}{dv} = 0$, till for q-lines of very low degree, for which as we shall presently see, the number of points of contact has again descended to two, the whole bears the character of a point of contact lying on the liquid side.

But something special may be remarked about the two inner points of contact of the four found on the above q-line. When the q-line descends in degree, these points will approach each other, and they will coincide on a certain q-line. Then we have again a plaitpoint. In this case neither $\left(\frac{d^2v}{dx^2}\right)_q$, nor $\left(\frac{d^2v}{dx^2}\right)_p$ need reverse its sign because these quantities have always the same sign for each of the two points of contact which have not yet coincided, i. e. in this case the positive sign. But in this case, too, there is again besides contact, also intersection of the p- and q-lines. On the left of this plaitpoint the q-line lies at larger volumes, on the right on the other hand at smaller volumes than the p-line, the latter changing its course soon after again from one going to the right into one going to the left.

This plaitpoint, however, is not to be realised. With the two plaitpoints discussed above all the p-line and all the q-line, at least in the neighbourhood of that point, lie outside the spinodal curve, and so in the stable region. In this case they lie within the unstable region.

Summarizing what has been said about fig. 8, we see that there is a group of q-lines which cut the spinodal curve in four points. The outside lines of this group pass through plaitpoints. That with the highest value of q passes through the plaitpoint that is to be realised; that with the lowest value of q passes through the plaitpoint that is not to be realised. All the q-lines lying outside this group intersect

the spinodal curve only in two points. If, however, the temperature chosen should lie above $(T_k)_2$ the q-lines of still higher degree than of that, passing through the vapour-liquid-plaitpoint, will no longer cut the spinodal curve.

And finally one more remark on the spinodal curve, which may occur in the case of fig. 8. By making the line $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ intersect, we have a region, in which both $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ is negative. In such a region the product of these quantities is again positive, and it may become equal to $\left(\frac{d^2\psi}{dxdv}\right)^2$. If this should be the case, it takes again place in a locus which forms a closed curve. Within this region there is then again a portion of the spinodal curve which is quite isolated from the spinodal curve considered. With regard to the p- and q-lines this implies, that there both $\frac{dv}{dx_p}$ and $\frac{dv}{dx_q}$ is negative; and so that contact is not impossible. Such a portion of a spinodal curve encloses then a portion of the ψ-surface which is concave-concave seen from below. If we consider the points lying within the spinodal curve as representing unstable equilibria, the points within this isolated portion of the spinodal curve are a fortiori unstable. The presence of such a portion of a spinodal curve not being conducive to the insight of the states which are liable to realisation, we shall devote no more attention to them.

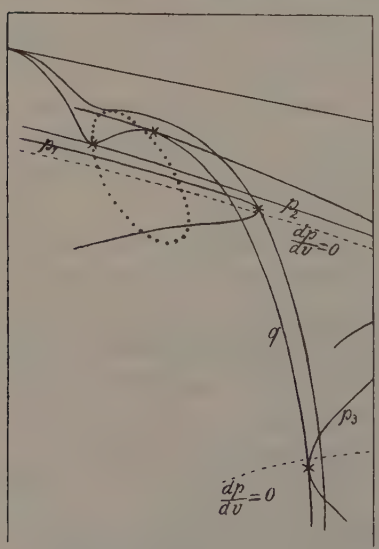

Fig. 8.

It appears from this description and from the drawing (fig. 8) that in this case the spinodal curve has a more complicated course than it would have if the curve $\frac{d^2\psi}{dx^2} = 0$ did not exist. It has a portion on the liquid side in which it is forced towards smaller volumes. There is, however, no reason to speak here of a longitudinal plait. We might speak of a more or less complicated plait here. But we shall only use the name of longitudinal plait, when we meet with a portion that is quite detached from the

ordinary plait, which portion will then on the whole run in the direction of the v-axis.

There remains an important question to be answered: "What happens to the spinodal curve and to the plaitpoints with increase of temperature?"

At the temperature somewhat higher than $(T_k)_2$ there exist 3 plaitpoints in the diagram. 1. The realisable one on the side of the liquid volumes. 2. The hidden plaitpoint also on the side of the liquid volumes. 3. The realisable vapour-liquid plaitpoint. Let us call them successively P_1, P_2 and P_3. Now there are two possibilities, viz. 1. that with rise of the temperature P_1 and P_2 approach each other and coincide, and the plait has resumed its simple shape before P_3 disappears at $T=(T_k)_1$; and 2. that with rise of T the points P_2 and P_3 coincide and disappear, and also in that case the plait has resumed a simple shape. In the latter case, however, the plaitpoint is to be expected at very small volumes, and so also at very high pressure. Then, too, all heterogeneous equilibria have disappeared at $T=(T_k)_1$. Perhaps there may be still a third possibility, viz. when the locus $\frac{d^2\psi}{dx^2}=0$ would disappear at a temperature higher than $(T_k)_1$. Besides the plaitpoint P_1 another new plaitpoint would then make its appearance at $T=(T_k)_1$ on the side of the first component. This would transform the plait into an entirely closed one, and only above the temperature, at which $\frac{d^2\psi}{dx^2}=0$ vanishes, all heterogeneous equilibria would have disappeared.

Let us now briefly discuss these different possibilities. We shall restrict ourselves to the description of what happens in those cases, and at least for the present leave the question unsettled on what properties of the two components it depends whether one thing or another takes place. If P_1 and P_2 coincide, the portion of the locus $\frac{d^2\psi}{dx^2}=0$ which we have drawn in fig. 8 for smaller volumes than that of $\frac{d^2\psi}{dv^2}=0$, must have got entirely or almost entirely within the region where $\frac{d^2\psi}{dv^2}$ is negative in consequence of the rise of temperature, or the whole locus $\frac{d^2\psi}{dx^2}=0$ may have disappeared with rise of T.

Now at P_1 in the previously given equation:

$$dv_p - dv_q = \frac{1}{1.2.3}\left\{\left(\frac{d^3v}{dx^3}\right)_p - \left(\frac{d^3v}{dx^3}\right)_q\right\} dx^3$$

the factor of dx^3 is negative, but at P_2 this factor is positive. If the points P_1 and P_2 coincide, this factor $= 0$. With coincidence of these plaitpoints, called *heterogeneous* plaitpoints by KORTEWEG, besides $\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$ and $\left(\frac{d^2x}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$, also $\left(\frac{d^3v}{dx^3}\right)_p = \left(\frac{d^3v}{dx^3}\right)_q$.

If P_1 and P_3 coincide, $\frac{d^2\psi}{dv^2} = 0$ has contracted with rise of temperature. Also $\frac{d^2\psi}{dv^2} = 0$ contracts with rise of the temperature and is displaced as a whole, as I hope to demonstrate further. But the contraction of $\frac{d^2\psi}{dv^2} = 0$, whose top moves to the left, happens relatively quicker, so that e.g. the top falls within the region in which $\frac{d^2\psi}{dx^2}$ is negative. The existence of the point P_2 requires that $\left(\frac{dv}{dx}\right)_q$ is positive. The point P_2 lies on the right of $\frac{d^2\psi}{dx^2} = 0$ and above $\frac{d^2\psi}{dv^2} = 0$. If the top of $\frac{d^2\psi}{dv^2} = 0$ lies within the curve $\frac{d^2\psi}{dx^2} = 0$, neither P_2 nor P_3 can exist any longer. Before this relative position of the two curves they have, therefore, already disappeared in consequence of their coinciding. Also in this case the coincidence of *heterogeneous* plaitpoints holds. At P_2 the factor of dx^3 was positive, and at P_3 this factor is negative. In case of coincidence $\left(\frac{d^3v}{dx^3}\right)_p = \left(\frac{d^3v}{dx^3}\right)_q$. With further rise of T, however, the top of $\frac{d^2\psi}{dv^2} = 0$ will have to get again outside the region where $\frac{d^2\psi}{dx^2}$ is negative. The curve $\frac{d^2\psi}{dx^2} = 0$, namely, cannot extend to $x = 0$, and the curve $\frac{d^2\psi}{dv^2} = 0$ at $T = (T_k)$, has its top at $x = 0$. We draw from this the conclusion, that

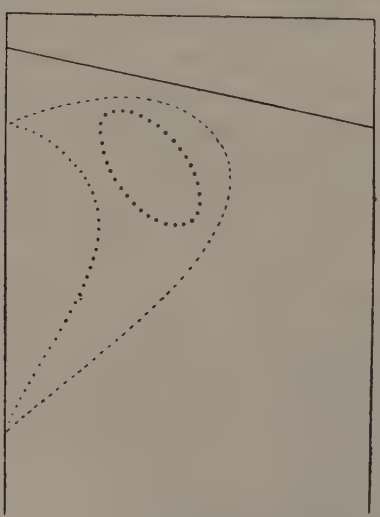

Fig. 9.

with continued increase of temperature the curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ will no longer intersect, but will assume the position indicated by fig. 9.

The spinodal line runs round the two curves, and so in consequence of the presence of $\frac{d^2\psi}{dx^2}=0$ it is forced to remain at an exceedingly large distance from the curve $\frac{d^2\psi}{dv^2}=0$. The question may be raised whether the spinodal curve cannot split up into two separated parts, one part enclosing the curve $\frac{d^2\psi}{dv^2}=0$, the other part passing round $\frac{d^2\psi}{dv^2}=0$. The answer must then be: probably not. In the points between the two curves $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ are indeed, positive, but still small, whereas $\frac{d^2\psi}{dx\,dv}$ does not at all occur in the figure, and will, therefore, in general, be large. Now if the temperature at which $\frac{d^2\psi}{dx^2}=0$ disappears, should lie above $(T_k)_1$, $\frac{d^2\psi}{dv^2}=0$ shifts to the left, till it leaves the figure, and the spinodal curve is closed at $x=0$ and $T=(T_k)_1$, and the new plaitpoint makes its appearance, which we mentioned above. From this moment we have a spinodal curve with two realisable plaitpoints. The graphical representation of the curvature of the p- and the q-lines is in this case very difficult, because both groups of lines have only a slight curvature. If, however, we keep to the rule, that the p- and the q-lines envelop the spinodal curve at realisable plaitpoints, we conclude that the value of $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ is positive in P_1, and negative in the other plaitpoint. When these points, called *homogeneous* plaitpoints by KORTEWEG, coincide, $\left(\frac{d^2v}{dx^2}\right)_p=\left(\frac{d^2v}{dx^2}\right)_q=0$. Above the temperature at which this takes place, the p- and the q-lines have no longer any point of contact. In consequence of the disappearance of the locus $\frac{d^2\psi}{dv^2}=0$, the course of the p-lines has become chiefly from left to right, so in the direction of the x-axis. On account of the disappearance of the locus

$\frac{d^2\psi}{dx^2} = 0$ the course of the q-lines has also been simplified, and at least with a volume which is somewhat above the limiting volume, they run chiefly in the direction of the v-axis.

Many of the results obtained about the course of the spinodal curve, and about the place of the plaitpoints, at which we have arrived in the foregoing discussion by examining the way in which the p- and the q-lines may be brought into mutual contact, may be tested by the differential equation of the spinodal line. This will, of course, also be serviceable when we choose another region than that discussed as yet.

From :

$$\frac{d^2\psi}{dv^2}\frac{d^2\psi}{dx^2} - \left(\frac{d^2\psi}{dxdv}\right)^2 = 0.$$

we derive:

$$\left\{\frac{d^2\psi}{dx^2}\frac{d^2\psi}{dv^2} + \frac{d^2\psi}{dv^2}\frac{d^3\psi}{dx^2dv} - 2\frac{d^2\psi}{dxdv}\frac{d^3\psi}{dxdv^2}\right\}dv +$$

$$+ \left\{\frac{d^3\psi}{dx^3}\frac{d^2\psi}{dv^2} + \frac{d^2\psi}{dx^2}\frac{d^3\psi}{dxdv^2} - 2\frac{d^2\psi}{dx^2}\frac{d^3\psi}{dx^2dv}\right\}dx +$$

$$+ \left\{-\frac{d^2\eta}{dx^2}\frac{d^2\psi}{dv^2} - \frac{d^2\eta}{dv^2}\frac{d^2\psi}{dx^2} + 2\frac{d^2\eta}{dxdv}\frac{d^2\psi}{dxdv}\right\}dT = 0.$$

We arrive at the shape of the factor of dT by considering that from:

$$d\varepsilon = T\,d\eta - p\,dv + q\,dx$$

follows :

$$d\psi = -\eta\,dT - p\,dv + q\,dx$$

so that $\left(\frac{d\psi}{dT}\right)_{v,x} = -\eta$ and so $\frac{d^2\psi}{dTdv^2} = -\left(\frac{d^2\eta}{dv^2}\right)_{x,T}$ etc.

This very complicated differential equation may be reduced to a simple shape.

Let us for this purpose first consider the factor of dv. By substituting in it the quantity $\frac{\left(\frac{d^2\psi}{dxdv}\right)^2}{\frac{d^2\psi}{dv^2}}$ for $\frac{d^2\psi}{dx^2}$, and $\left(\frac{dv}{dx}\right)_p$ for $-\frac{\frac{d^2\psi}{dxdv}}{\frac{d^2\psi}{dv^2}}$ this factor becomes :

$$\frac{d^2\psi}{dv^2}\left\{\frac{d^3\psi}{dv^3}\left(\frac{dv}{dx}\right)_p^2 + 2\frac{d^3\psi}{dxdv^2}\left(\frac{dv}{dx}\right)_p + \frac{d^2\psi}{dx^2dv}\right\}.$$

From $p = -\frac{d\psi}{dv}$ we derive :

$$\frac{d^2\psi}{dv^2}\left(\frac{dv}{dx}\right)_p+\frac{d^2\psi}{dxdv}=0$$

and

$$\frac{d^2\psi}{dv^2}\left(\frac{d^2v}{dx^2}\right)_p+\left\{\frac{d^3\psi}{dv^3}\left(\frac{dv}{dx}\right)_p^2+2\frac{d^3\psi}{dv^2dx}\left(\frac{dv}{dx}\right)_p+\frac{d^3\psi}{dx^2dv}\right\}$$

from which appears that we can write the factor of dv in the form of:

$$-\left(\frac{d^2\psi}{dv^2}\right)^2\left(\frac{d^2v}{dx^2}\right)_p.$$

We might proceed in a similar way with regard to the factor of dx, but we can immediately find the shape of this factor by substituting the quantity x for v and q for p in the factor of dv. We find then:

$$-\left(\frac{d^2\psi}{dx^2}\right)^2\left(\frac{d^2x}{dv^2}\right)_q.$$

As long as we keep T constant, and this is necessary for the course of a spinodal curve, the differential equation, therefore, may be written:

$$-\left(\frac{d^2\psi}{dv^2}\right)^2\left(\frac{d^2v}{dx^2}\right)_p dv-\left(\frac{d^2\psi}{dx^2}\right)^2\left(\frac{d^2x}{dv^2}\right)_q dx=0.$$

By taking into account that $\left(\frac{d^2x}{dv^2}\right)_q=-\left(\frac{dx}{dv}\right)_q^3\left(\frac{d^2v}{dx^2}\right)_q$, we obtain after some reductions which do not call for any explanation, the simple equation:

$$\left(\frac{dv}{dx}\right)_{spin}=\left(\frac{dv}{dx}\right)_{p=q}\frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}.$$

As a first result we derive from this equation the thesis, that $\left(\frac{dv}{dx}\right)_{spin}$ and $\left(\frac{dv}{dx}\right)_{p=q}$ must have the same sign, if $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have the same sign and vice versa. Thus on the vapour side in fig. 7 $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ have always reversed sign, and $\left(\frac{dv}{dx}\right)_{p=q}$ being negative, $\left(\frac{dv}{dx}\right)_{spin}$ is negative on the vapour branch of the spinodal curve. Reversely the curvatures of the p and q-lines have the same sign on the liquid side, and $\left(\frac{dv}{dx}\right)_{bin}=\left(\frac{dv}{dx}\right)_{p=q}=$ positive. If, however,

$\left(\frac{d^2v}{dx^2}\right)_q$ should have been indeed negative there, as was accidentally represented in point 2 of the spinodal curve, the spinodal curve runs towards smaller volumes with increasing value of x. So if there occur points with maximum or minimum volume on the spinodal curve, $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in those points. If on the other hand $\left(\frac{dv}{dx}\right)_{spin}$ is infinitely large, which occurs in the case under consideration when the spinodal curve is closed on the right side for $T > (T_k)_2$ then $\left(\frac{d^2v}{dx^2}\right)_p$ must be $= 0$, and so the p-line must have a point of inflection in such a point, to which we had moreover already concluded before in another way. A great number of other results may be derived from this differential equation of the spinodal line. We shall, however, only call attention to what follows. In a plaitpoint $\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q}$. For a plaitpoint it follows from this that $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$.

If for a point of a spinodal curve $\left(\frac{dv}{dx}\right)_{spin}$ is indefinite, both $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ must be equal to 0. This takes place in two cases: 1. in a case discussed above when the whole of the spinodal line is reduced to one single point. 2. when a spinodal line splits up into two branches, as is the case for mixtures for which also T_k minimum is found. In the former case the disappearing point has the properties of an isolated point, in the second case of a double point.

In the differential equation of the spinodal line the factor of dT may be written:

$$-\frac{1}{T}\left\{\left(\frac{d^2T\eta}{dx^2}\right)_{vT}\frac{d^2\psi}{dv^2} - 2\left(\frac{d^2T\eta}{dxdv}\right)_T\frac{d^2\psi}{dxdv} + \left(\frac{d^2T\eta}{dv^2}\right)_{Tx}\frac{d^2\psi}{dx^2}\right\}$$

and by putting $\varepsilon - \psi$ for $T\eta$ it may be reduced to:

$$-\frac{1}{T}\left\{\frac{d^2\psi}{dv^2}\frac{d^2\varepsilon}{dx^2} - 2\frac{d^2\psi}{dxdv}\frac{d^2\varepsilon}{dxdv} + \frac{d^2\psi}{dx^2}\frac{d^2\varepsilon}{dv^2}\right\}$$

or to

$$-\frac{1}{T}\frac{d^2\psi}{dv^2}\left\{\frac{d^2\varepsilon}{dv^2}\left(\frac{dv}{dx}\right)^2_{p=q} + \frac{d^2\varepsilon}{dxdv}\left(\frac{dv}{dx}\right)_{p=q} + \frac{d^2\varepsilon}{dx^2}\right\}.$$

The factor by which $-\frac{1}{T}\frac{d^2\psi}{dv^2}$ is to be multiplied, occurs for the

first time in formula (4) Verslag K. A. v. W. Mei 1895, and at the close of that communication I have written this factor in the form:

$$-\frac{2a}{v}\left\{\left(\frac{1}{v}\frac{dv}{dx_v}-\frac{1}{2a}\frac{da}{dx}\right)^2+\frac{a_1a_2-a_{12}^2}{a^2}\right\},$$

from which appears that in any case when $a_1a_2 > a_{12}^2$, this factor is negative. Here, too, I shall assume this factor to be always negative, but I may give a fuller discussion later on.

In consequence of these reductions the differential equation of the spinodal curve may be written as follows:

$$\frac{d^2\psi}{dv^2}\left(\frac{d^2v}{dx^2}\right)_{pT}dv+\frac{d^2\psi}{dxdv}\left(\frac{d^2v}{dx^2}\right)_{qT}dx+\frac{dT}{T}\left(-\right)=0.$$

From this equation follows inter alia this rule concerning the displacement of the spinodal curve with increase of T, that on the side where $\left(\frac{d^2v}{dx^2}\right)_p$ is positive, the value of v with constant value of x, increases, and the reverse. So the two branches of a spinodal curve approach each other with increase of the temperature. But I shall not enter into a discussion of the further particulars which might occur when this formula is applied. By elimination of dv I shall only derive the differential equation of the spinodal line when we think it given by a relation between p, x and T. We find then:

$$\left(\frac{d^2v}{dx^2}\right)dp=\left(\frac{dp}{dx}\right)_{v,T}\left[\left(\frac{d^2v}{dx^2}\right)_{p,T}-\left(\frac{d^2v}{dx^2}\right)_{q,T}\right]dx+\frac{dT}{T}\left[(-)+T\left(\frac{dT}{dp}\right)_{v,x}\left(\frac{d^2v}{dx^2}\right)_{pT}\right]$$

for a plaitpoint the factor of dx disappears, and we find back the equation (4). Verslag K. A. v. W. Mei 1895, for the plaitpoint curve. At constant temperature we find for the spinodal curve:

$$\left(\frac{dp}{dx}\right)_{spin}=\left(\frac{dp}{dx}\right)_v\left\{1-\frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}\right\}.$$

(*To be continued*).

Physics. — *"The shape of the empiric isotherm for the condensation of a binary mixture"*. By Prof. J. D. VAN DER WAALS.

Let us imagine a molecular quantity of a binary mixture with a mass equal to $m_1(1-x)+m_2x_1$ at given temperature in a volume, so that part of it is in the liquid state, and the remaining part in the vapour state. Let us put the fraction which is found in the vapour state equal to y. The point that indicates the state of that mixture, lies then on a nodal curve which rests on the binodal curve. Let the end of the nodal line which rests on the liquid branch be denoted by the index 1, and the other end by the index 2. Let us represent the molecular volume of the end 1 by v_1, and the molecular volume of the other end by v_2, then when v represents the volume of the quantity which is in heterogeneous equilibrium:

$$v = v_1(1-y) + v_2 y$$

the constant quantity x being represented by:

$$x = x_1(1-y) + x_2 y.$$

From this we find:

$$dv = (v_2-v_1)\,dy + (1-y)\,dv_1 + y\,dv_2$$

and

$$0 = (x_2-x_1)\,dy + (1-y)\,dx_1 + y\,dx_2.$$

By elimination of dy we obtain the equation:

$$-dv = \frac{v_2-v_1}{x_2-x_1}\left\{(1-y)\,dx_1 + y\,dx_2)\right\} - (1-y)\,dv_1 - y\,dv_2.$$

Now in general $dv = \left(\frac{dv}{dx}\right)_p dx + \left(\frac{dv}{dp}\right)_x dp$. Let us apply this equation for the points 1 and 2 of the binodal curve, and let us take the course going from v_1 to v_1+dv_1 and from v_2 to v_2+dv_2 on the surface for the homogeneous phases. Then:

$$dv_1 = \left(\frac{dv_1}{dx_1}\right)_p dx_1 + \left(\frac{dv_1}{dp}\right)_{hom} dp,$$

and

$$dv_2 = \left(\frac{dv_2}{dx_2}\right)_p dx_2 + \left(\frac{dv_2}{dp}\right)_{hom} dp.$$

The quantities $\left(\frac{dv_1}{dx_1}\right)_p$ and $\left(\frac{dv_2}{dx_2}\right)_p$ must then be taken along an isobar.

If we substitute the values of dv_1 and dv_2 in the equation for dv, it becomes:

$$-dv = (1-y)\left\{\left[\frac{v_2-v_1}{x_2-x_1}-\left(\frac{dv_1}{dx_1}\right)_p\right]dx_1-\left(\frac{dv_1}{dp}\right)_{hom}dp\right\}+$$
$$+\quad y\quad\left\{\left[\frac{v_2-v_1}{x_2-x_1}-\left(\frac{dv_2}{dx_2}\right)_p\right]dx_2-\left(\frac{dv_2}{dp}\right)_{hom}dp\right\}$$

or

$$-\left(\frac{dv}{dp}\right)_{het}=(1-y)\left\{\left[\frac{v_2-v_1}{x_2-x_1}-\left(\frac{dv_1}{dx_1}\right)_p\right]\left(\frac{dx_1}{dp}\right)_{bin}-\left(\frac{dv_1}{dp}\right)_{hom}\right\}+$$
$$+\quad y\quad\left\{\left[\frac{v_2-v_1}{x_2-x_1}-\left(\frac{dv_2}{dx_2}\right)_p\right]\left(\frac{dx_2}{dp}\right)_{bin}-\left(\frac{dv_2}{dp}\right)_{hom}\right\}$$

Now the factor of $\left(\frac{dx_1}{dp}\right)_{bin}=\frac{v_{21}}{x_2-x_1}=\left(\frac{d^2\xi}{dx_1^2}\right)_{p,T}\left(\frac{dx_1}{dp}\right)_{bin}$, and we find:

$$-\left(\frac{dv}{dp}\right)_{het}=(1-y)\left\{\left(\frac{d^2\xi}{dx_1^2}\right)_{p,T}\left(\frac{dx_1}{dp}\right)^2_{bin}-\left(\frac{dv_1}{dp}\right)_{hom}\right\}+$$
$$+\quad y\quad\left\{\left(\frac{d^2\xi}{dx_2^2}\right)_{p,T}\left(\frac{dx_2}{dp}\right)^2_{bin}-\left(\frac{dv_2}{dp}\right)_{hom}\right\}\quad .\quad .\quad .\quad (1)$$

If we consider the beginning of the condensation, and so $y=1$, the above equation becomes:

$$-\left(\frac{dv}{dp}\right)_{het}=\left(\frac{d^2\zeta}{dx_2^2}\right)_{p,T}\left(\frac{dx_2}{dp}\right)^2_{bin}-\left(\frac{dv_2}{dp}\right)_{hom}$$

in which we must put $v_2=v$ and $x_2=x$. It appears from this equation, that never $-\left(\frac{dv}{dp}\right)_{het}=-\left(\frac{dv}{dp}\right)_{hom}$, and that there must therefore be a leap in the value of $-\frac{dv}{dp}$ or of $-\frac{dp}{dv}$ at the beginning of the condensation, unless there should be cases in which $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}\left(\frac{dx}{dp}\right)^2_{bin}$ is equal to 0. The only case in which this is so, is in the critical point of contact. There $\left(\frac{dp}{dx}\right)_{bin}=\infty$ and so $\left(\frac{dx}{dp}\right)_{bin}=0$. But then there is properly speaking no longer condensation, and the empiric isotherm has disappeared. We might think of a plaitpoint, because $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}=0$ in it, but on the other hand $\left(\frac{dp}{dx}\right)_{bin}=0$ and $\left(\frac{dx}{dp}\right)_{bin}=\infty$ there. If the limiting value of $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}\left(\frac{dx}{dp}\right)^2_{bin}$ or of $\frac{\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}}{\left(\frac{dp}{dx}\right)^2_{bin}}$ is sought, we find by differentiating numerator and deno-

minator twice with respect to x:

$$\frac{\left(\frac{d^2\zeta}{dx^2}\right)_{pT}}{\left(\frac{dp}{dx}\right)^2_{bin}} = \frac{\left(\frac{d^3\zeta}{dx^3}\right)_{pT}}{2\left(\frac{dp}{dx}\right)_{bin}\left(\frac{d^2p}{dx^2}\right)_{bin}} = \frac{\left(\frac{d^4\zeta}{dx^4}\right)_{p,T}}{2\left(\frac{d^2p}{dx^2}\right)^2_{bin}}.$$

In a plaitpoint, besides $\left(\frac{d^2\zeta}{dx^2}\right)_{p,T}$ also $\left(\frac{d^3\zeta}{dx^3}\right)_{p,T} = 0$, but $\left(\frac{d^4\zeta}{dx^4}\right)_{p,T}$ will have a value differing from 0, and so there is a leap in the value of $-\frac{dv}{dp}$ in a plaitpoint too.

As $-\left(\frac{dv}{dp}\right)_{hom}$ must always be positive, also $\left(-\frac{dv}{dp}\right)_{het}$ will always be positive and larger than $\left(-\frac{dv}{dp}\right)_{hom}$ or $\left(-\frac{dp}{dv}\right)_{hom} > \left(-\frac{dp}{dv}\right)_{het}$.

At the beginning of the condensation the empiric curve will ascend less steeply with decrease of volume than that for homogeneous phases.

There are cases in which $-\left(\frac{dv}{dp}\right)_{het} = \infty$, or $\left(-\frac{dp}{dv}\right)_{het} = 0$. 1. on the sides, so for $x = 0$ and $x = 1$. Then $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$ is infinite, and is represented by the principal term $\left(\frac{MRT}{x(1-x)}\right)$. 2. if on the binodal curve $\frac{dx}{dp}$ is infinite or $\frac{dp}{dx} = 0$; this takes place for those mixtures which behave as a simple substance.

If in equation (1) we put $y = 0$ and $v_1 = v$ and $x_1 = x$ we could derive the same conclusions for the end of the condensation.

The relation between $-\left(\frac{dp}{dv}\right)_{het}$ and $-\left(\frac{dp}{dv}\right)_{hom}$ at the beginning and at the end of the condensation, could be immediately derived by applying the equation:

$$dv = \left(\frac{dv}{dp}\right)_x dp + \left(\frac{dv}{dx}\right)_p dx$$

both for the surface of the homogeneous phases and for that of the heterogeneous phases. If we then take into consideration that $\left(\frac{dv}{dx}\right)_p$ on the heterogeneous surface is equal to $\frac{v_2 - v_1}{x_2 - x_1}$, we find:

$$\frac{v_3-v_1}{x_2-x_1}\,dx+\left(\frac{dv}{dp}\right)_{het}dp=\left(\frac{dv}{dx}\right)_p dx+\left(\frac{dv}{dp}\right)_{hom}dp,$$

and from this the former relation.

From the form for $\left(-\frac{dv}{dp}\right)_{het}$ in general, so not only at the beginning or at the end of the condensation, we see that the empiric isotherm can have an element in which it has an horizontal direction only when a nodal curve is intersected, at one or the other of whose ends $\left(\frac{dx}{dp}\right)_{bin}$ is infinitely large. But as neither the sides nor the nodal curve which runs parallel to the v-axis can be intersected, it would follow that the empiric isotherm can never run horizontally in one of its elements. There *are*, however, cases which form exceptions to this rule. First of all if we widen the idea empiric isotherm, and understand by it the section of a surface // v-axis with the derived surface of the ψ-surface, also in the case of a complex plait. Then there are also nodal curves to points in which the binodal curve passes through the spinodal, and where therefore $\left(\frac{dx}{dp}\right)_{bin}=\infty$. But as such equilibria are hidden equilibria, they cannot be realised in spite of this. Instead of this we have rectilinear intersection of the surface // v-axis with the three phase triangle, and in this part $\left(\frac{dv}{dp}\right)_{het}$ is, of course, again infinitely large. But secondly, and this is a case which might, indeed, be realised, the binodal curve has a point in which $\left(\frac{dx}{dp}\right)_{bin}=\infty$, when this point is a plaitpoint which with increasing or decreasing temperature will become a hidden plaitpoint. This is a limiting form of the first mentioned case, in which the three phase triangle was intersected. Then the three phase triangle has contracted to a single line, and the above mentioned straight line has contracted to a single point. Then there is, of course, a point of inflection of the empiric isotherm in that point. With larger volumes it is curved negatively, with smaller volumes positively.

Physics. — "*Isotherms of di-atomic gases and their binary mixtures. VI. Isotherms of hydrogen between* — 104° C. and — 217° C." By Prof. H. KAMERLINGH ONNES and C. BRAAK. Comm. N°. 97*a* from the Physical Laboratory at Leiden.

(Communicated in the meeting of December 29th 1906).

§ 1. *Introduction.*

The investigation treated in this Communication forms part of the investigation on the equation of state of hydrogen, which has been in progress at Leiden for many years. [1])

With that part of our measurements [2]) which we now deem fit for publication, we have more directly carried on the work that H. H. FRANCIS HYNDMAN had already done with one of us (K. O.) before 1904, so that, though all the observations, one for this, another for that reason, but always for the purpose of reaching the desired accuracy (which, we may add, was increased in the course of the investigation) have been repeated, an important share of the final success of the measurements is due to the said investigator.

The results obtained by us furnish data for applying the correction of the readings of the hydrogen thermometer to the absolute scale experimentally (see the following communication), and for determining the deviation between the net of isotherms of hydrogen and that of the mean reduced equation of state (see Comm. N°. 71, June 1901 and Comm. N°. 74, Arch. Néerl. 1901) [3]). The points determined in

[1]) In Comm. N°. 69 (March 1901), where the apparatus have been described which were used in this investigation, the Communications referring to this subject, have been mentioned. Since then the isotherm for 20° C. to 60 atms. was given in Comm. N°. 70 (May and June 1901) with the accuracy of which the open standard-manometer (Comm. N°. 44 Oct. 1898) and the closed standard manometers (Comm. N°. 50 June 1899) admit, which investigation is carried on in Comm. N°. 78 (March 1902) for the isotherms of hydrogen at 20° C. and 0° C., which have been determined with the apparatus that have also been used for this investigation. The suitability of these apparatus for accurate determinations of isotherms has been shown in Comm. N°. 78, and is confirmed by this Communication for low temperatures. Several communications e. g. N°s. 83, 84, 94*b* and 94*f*, further 85 and 95*b*, finally N°s. 89, 93 and 95 are more or less in connection with this investigation, the great importance of which, if accurately carried out, is demonstrated in Suppl. N°. 9.

[2]) We soon hope to publish the results of measurements at higher pressures and lower temperatures, and also those of supplementary determinations at lower pressures.

[3]) Definitive values for the virial coefficients B and C (§ 12 contains only provisional values) from which the difference with those according to the reduced equation may follow, are given in the following communication.

the net of isotherms are only few in number, but these few points have been determined with particular care, so that, so to say, they form normal places in the examined region of the equation of state, with which without preliminary adjustment we may set about the calculation of individual virial coefficients. Characteristic of them is that every group of such normal places obtained by determinations with the piezometer and manometer (see Comm. N°s. 69 and 78) lies really on the same isotherm (that of about — 104°, — 136°, — 183°, —195°, —205°, —213° and —217°), and that on these same isotherms every time a point has been obtained at small density by a determination with the hydrogen thermometer (see Comm. N°. 95^{e} Oct. 1906). The great difficulty [1]) of this investigation lies in obtaining the required constancy and stability of the low temperatures. Accordingly the arrangement of reliable cryostats was made a separate subject of investigation at Leiden. (cf. Comm. N°s. 83 and 94).

This investigation comprises three series of piezometer-determinations at densities respectively about 70, 160, and 300 times the normal. [2]) Several of the observations mentioned here lie in the neighbourhood of the curve of the minima of pv. They enable us to determine the shape of this curve pretty accurately (see § 13).

We confine ourselves in this communication to our observations themselves. A discussion of them, also in connection with the results of other observers, will be given in a following communication.

§ 2. *Survey of the apparatus used.*

a. On Pl. I in fig. 1 we find a schematic [3]) representation of the system of the apparatus for measurements and auxiliary arrangements, excepted those which serve for keeping constant the temperature in the cryostat. The compression apparatus A is the same as that mentioned in Comm. N°. 84 (March '03). For the meaning of the system of tubes, cocks and other parts we may refer to Comm. N°. 69 and N°. 84. The same figures have been used, except that in this communication c_1 is used for the cock which admits the

1) Witkowski, whose important investigation on the expansion of hydrogen (Bulletin de l'Académie des Sciences de Cracovie 1905) had already appeared before the experiments mentioned in this communication had been completed, already mentions this as an explanation for the fact, that he has dropped the direct determination of isotherms at temperatures lower than — 147°.

2) The limits are chiefly given by the pressure under which the gas stands; they are about 20 and 60 atms.

3) The individual apparatus are represented on the same scale, the connections schematically.

compressed air, and c_2 for the cock which shuts off the level glass. Of the compression tube, provided with the system of cocks, mercury-reservoir and level-glass belonging to it a front-view is given in fig. 3 of Pl. I. The piezometer with the connections g_1 and g_2 has been represented in detail in fig. 2 of Pl. I.

The arrangement of the cryostat B which has served for the determinations mentioned in this communication, is described in Comm. N°. 94^d.

For the description of the apparatus serving for keeping the temperature in the cryostat constant, we may also refer to this last communication. Fig. 4 of Pl. I may also serve for elucidating this description for the special case that our piezometer is placed in the cryostat.

The pressure is conveyed (see fig. 1, Pl. I) from the compression-tube to the manometer along c_{11}, c_8, c_{12}, c_{13}, c_{14} and c_{15}. By closing and opening c_{12} the differential-manometer E [1]) may be shunted in and out. By means of the cocks c_8 and c_{13} it may be shut off from the rest of the pressure-conduit, when great differences in pressure are brought about, or are to be feared. [2]) [3]). The apparatus are placed in two rooms as has been indicated in the figure by a dotted line. By closing one of the cocks c_{13} and c_{14} the two parts may be treated as independent systems. This was done when the manometer was compared with the open manometer connected at c_{17}. The manometer C is the same as served for the investigations of Comm. N°. 78. The reservoir D serves, if necessary, for eliminating the injurious influence of small leaks, for which purpose it is placed in ice. At c_{16} it can be coupled to the system. In the experiments of this communication there was no need to use it [4]). The pressure is exerted by compressed air, which enters through c_1 and c_{19} along the drying tubes F and G; and is regulated by blowing off along c_{24}. The cocks c_{15}, c_{18}, c_{20}, c_{21}, c_{22} and c_{23} have analagous meaning to c_{11}, c_7, c_3, c_4, c_5 and c_6.

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[1]) This manometer, which was formerly used with the open standard-manometer, (see C fig. 1 Comm. N°. 44) and had now been removed to the piezometer, was of great use for finding leaks.

[2]) A couple of mercury-receptacles, which served for receiving the mercury that might overflow, have not been represented in the figure.

[3]) The system which we have so far described and which belongs to the piezometer, is placed in one of the rooms of the laboratory, situated in the immediate neighbourhood of the cryogen department. The remaining apparatus which chiefly belong to the manometer are erected in the room with the standard-manometer.

[4]) The adjustment of trays of oil for the different couplings rendered the search for leakages so easy, that an injurious leak needed never to remain.

All couplings of the conducting tubes in which air is to be kept at constant pressure, have been placed (cf. the plate to Comm. N°. 94*b*) in trays filled with oil, according to what has been said in Comm. N°. 94*b*.

b. With regard to the means for keeping a constant temperature in the cryostat, the system of pumps and auxiliary arrangements for the regulation of the temperature, belonging to the circulation of oxygen, has been represented in fig. 4 of Pl. I. For a description we refer to Comm. N°. 94.

Some particulars about the ethylene circulation used for the determinations of Series I, are to be found in Comm. N°. 94*f* XIII § 1.

§ 3. *The manometer.*

The pressure measurements were performed by means of the closed auxiliary manometer described in Comm. N°. 78*c*. As a comparison of this manometer made in 1904 with the standard manometer A IV (of Comm. N°. 78 § 17), yielded an unsatisfactory result, and led us to expect that the auxiliary manometer was no longer reliable, it was compared at four points with the open standard manometer, to which the improvements mentioned in Comm. N°. 94*b* were applied [1]). The results of this comparison have been combined in the subjoined table.

Column *C* like column *C* of table XVII of Comm. N°. 78*c* represents the reading of the pressure determined with the open manometer (Comm. N°. 44). Every value is the mean of two observations. Column *F* gives the pressure read by means of our closed auxiliary manometer. Each of the values has been obtained as a mean from three observations. In the calculation the calibration derived in Comm. N°. 78*c* has been used. In column *G* the difference of the columns *F* and *G* is represented, column *H* contains this same difference expressed in the numbers of column *C* as unity. The pressure given by the auxiliary manometer appears to be too high for all pressures observed. It was obvious to ascribe this to a too high value assumed for the normal volume [2]).

If we take the mean of the values in column *H*, we find 0.00087. If we diminish the normal-volume and so also the pressures by this part of the original amount, the differences represented in

[1]) In the investigations with this manometer of Comm. N°. 70 the total absence of leaks was rare; here, however, it was easily brought about. Also the improved coupling of the steel capillaries to the glass-capillaries of the open manometer by platinizing proved satisfactory. (See Comm. N°. 94*b*).

[2]) In connection with this diminution of the normal volume see also Comm. N°. 95*e*, § 11.

column K remain between the indications of the auxiliary manometer and the open standard manometer. These differences, considerably smaller than those in table XVII of Comm. N°. 78, remain within the limits of accuracy fixed for this investigation, and justify us to estimate the mean error in the pressure measurements at $\pm \frac{1}{3000}$.

In the following the pressures have been calculated with this new value of the normal volume.

TABLE I. Manometer.

C	F	G	H	K
24.247	24.264	+ 0.017	0.00070	— 0.00017
36.290	36.333	+ 0.043	0.00120	+ 0.00033
47.960	48.004	+ 0.044	0.00092	+ 0.00005
60.022	60.061	+ 0.039	0.00065	— 0.00023

§ 4. *The piezometers and auxiliary apparatus.*

The piezometer used in the first series for the observations at a density 70 and the temperatures —104°, —136°, —183°, —195°, was of about the same dimensions as that used for the observations of Comm. N°. 78. In the subjoined table, just as in the corresponding table II of that communication, the dimensions are given to facilitate a survey of the amount and the influence of the many corrections.

TABLE II. Data H_2, Series I.

$U_1 = 6.4110$ cm³. $\beta_1 = 5.0 \cdot 10^{-6}$ [1]

$U_2 = 0.0530$ » $\beta_4 = 4.7 \cdot 10^{-6}$

$V_3 = U_3 = 1.198$ »

$V_4 = 6.0174$ »

U_4 has been determined from a calibration table

$V_5 = 576.077$ cm³.

$v' = 0.722$ » per cm.

[1]) The values of β given here have been determined for the ordinary temperature and those for lower temperatures have been put equal to them. We hope soon to determine β also for lower temperatures.

The stem b_4 (see Pl. II Comm. N°. 69), on which the volume U_4 is read, was 30 cm. long in order to enable us to determine every time three points on the isotherm which did not lie too near each other [1]). In others of our piezometers it was taken still longer.

For the series II and III a piezometer of larger dimensions was used.

The necessity of the use of a larger gas-volume for determinations at densities higher than 120 times the normal has already been mentioned in § 19 of Comm. N°. 84. The volumenometer described there was not used, but just as in Series I the normal-volume was determined in the piezometer itself.

As in the preceding table the dimensions of the piezometer are given here.

TABLE III. Data H_3, Series III.

$U_1 =$ 5.1583 cm³.	$\beta_1 = 3.7 \cdot 10^{-6}$
$U_2 =$ 0.0382 »	$\beta_4 = 4.7 \cdot 10^{-6}$
$V_3 = U_3 =$ 1.407 »	
$V_4' =$ 10.9645 »	
$U_4 =$ (see preceding table)	
$V_5 =$ 2063.30 cm³.	
$v' =$ 1.617 » per cm.	

In Series II the piezometer-reservoir had a volume of 10.343 cM³, but for the rest it had the same dimensions as in Table III.

To detect any escaping of gas during the measurements at high pressure in consequence of leakages at the connections g_2 and g_3 (see Pl. II Comm. N°. 69), cylindric glass oil-trays were placed round these couplings (see Pl. I fig. 2) which enabled us to discover immediately even the slightest leakage; everywhere the oil-trays rendered excellent services, but here they were of the greatest importance for obtaining reliable results [2]).

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[1]) They may serve, inter alia, to give us information about the curvature and the inclination of the isotherms at the middle point.

[2]) Once the oil-trays near the couplings g_1 and g_2 rendered good services, when before the determinations of Series III gas escaped in consequence of the nut g_2 being imperfectly screwed on. From a determination of the normal-volume made immediately afterwards, it proved to have changed so much that the previous determinations had to be rejected.

§ 5. *The hydrogen.*

The filling was accomplished for Series III with all the improvements described in Comm. N°. 94^e § 2. For the first series the purification by means of cooling in liquid air was not yet applied, in the second series it was, but without application of high pressure.

§ 6. *The temperatures.*

The temperatures t_4 and t_3 respectively of the divided stem b_1 and the steel capillary g_1 (see Comm. N°. 69 Pl. II) were determined in the same way as in Comm. N°. 78 § 13. In series I three thermometers were placed along the steel capillary, and one at the part of the glass capillary f_2 that remained outside the cryostat. The refrigerating action of the cryostat proving to be very slight even in the immediate neighbourhood, only three thermometers were used in the following two series, two at the ends and one in the middle of the steel capillary. The influence of an error of 1° C. in the temperature of the capillary (comp. Comm. N°. 78 § 13) is only $\frac{1}{4000}$ of the total compressed volume at — 100° and $\frac{1}{10000}$ at —200°. For the temperature of the glass capillary we assumed here that indicated by the thermometer at the end of the steel capillary. This simplification is the more admissible as the temperature in the cryostat is lower, and hence the volumes outside it contain less gas.

The temperature of the glass capillary in the cryostat has been determined in the same way as was followed in the investigations with the hydrogen thermometer mentioned in Comm. N°. 95^e. As the arrangement of the cryostat was the same in the two cases, and the measuring-apparatus placed in it had almost the same form, there was no objection to start from the previously found data for the determination of the temperature of the capillary. (see Comm. N°. 95^e § 4). This method gives sufficient accuracy, as, reasoning in a similar way to that followed in the said communication, we arrive at the result, that an error of 50° in the temperature of the part of the stem that is taken into consideration still gives a negligible error in the final result, viz. less than $\frac{1}{5000}$.

The temperature t_1 of the piezometer-reservoir was determined by means of the resistance-thermometer, which (cf. Comm. N°. 95^c) had beforehand been compared with the hydrogen-thermometer.

They differ little from those at which the calibration of the resistance-thermometer took place. Hence the reductions are simple and may be effected with great accuracy.

The temperatures were not calculated directly from the resistance

formula of comm. N°. 95 § 6, but they were based on the separate readings of the hydrogen-thermometer, because the latter must also serve as points of the isotherms. From the above mentioned formula $\frac{dt}{dw}$ was determined, and by the aid of this factor the reduction was effected.

The difference of temperature for which the reduction was made amounting to less than 0.°3, this method of calculation is perfectly sufficient; only for the temperature of — 135°.71, where the difference amounts to 4°, another correction of 0.°01 was required.

In the subjoined table[1]) the method of calculation has been represented for one determination of the temperature. The first column contains the observed resistance W, in the following column W_c represents the resistance at which the resistance-thermometer has been compared with the hydrogen-thermometer (of comm. N°. 95c Table I § 6), and T represents the corresponding reading of the hydrogen-thermometer. From the value $\frac{dt}{dw}$ and $W - W_c$ follows now the temperature-correction Δt which is to be added to T_c in order to give t_1 on the hydrogen-thermometer-scale.

TABLE IV. Temperature of the bath during observation N°. 7 of Series III.

W	W_c	T_c	$\frac{dt}{dw}$	Δt	t_1
17.295	17.290	— 212°.832	1.750	+ 0°.009	— 212°.82

§ 7. *The measurements.*

At the beginning and the end of every series the normal-volume was determined in the way described in Comm. No. 78 § 12, only with this difference that in the series mentioned here every determination of the normal-volume was supplemented with a reading in the U-tube b_2 and one of the barometer. In this way two determinations were generally made before and after every series. The values found before and after every series, differ nowhere more than $\frac{1}{2000}$.

The tables V and VI are analogous to the tables VII and VIII of Comm. N°. 78. In the former the results are represented referring to

[1]) The difference of the numbers in this table with those of the Dutch text is due to an improved calculation. The influence of this improvement enters also in some numbers of the last part of this communication.

the determination of the normal-volume for series III, the latter comprises the three series.

TABLE V. Normal volume H_2, Series III.

N°.	Volume.	Pressure.	$p\,v_A$	Mean.	Mean.	Difference.
1	1955.78	75.546	1945.56	1945.58	1945.73	— 0.17
2	1955.82	75.545	1945.60			— 0.13
9	1961.39	75.342	1945.87	1945.87		+ 0.14
10	[1962.04	75.327	1946.13 [1])			+ 0.40]
11	[1962.31	75.317	1946.14			+ 0.41]

TABLE VI. Normal volumes H_2.

Determinations.		Before.	After.	Mean.	Difference.
Series I	N°. 1	544.74	544.82	544.78	— 0.05
	2				— 0.02
	10				+ 0.02
	11				+ 0.07
Series II	1	1945.73	1946.10	1946.16 [2])	— 0.60
	2				— 0.46
	3				— 0.23
	11				+ 0.05
	12				— 0.18
	21	1946.10	1946.64		+ 0.39
	22				+ 0.58
	23				+ 0.47
Series III		1945.58	1945.87	1945.73	see Table V

[1]) The two last determinations have been left out of account, though they show but slight deviations, because on account of variations of temperature in the room a certain cause could be assigned for the apparent rise of the normal-volume.

[2]) A determination of the normal volume was made in this series both before and after, and also between the determinations at high pressure. The value given here is the mean from these three determinations.

As far as the pressure permitted, three points were chosen in every series on every isotherm for the determinations of the isotherms ascending with about equal differences of density, which offers advantages for the calculation of the virial coefficients (see § 12). The readings were adjusted at these points by bringing the mercury at the bottom, in the middle and at the top of the divided stem b_4. By way of control the two points in the middle and at the bottom of the stem were for some determinations determined once more with decreasing pressure.

For every determination we waited till both the temperature and the pressure were constant, and we could assume that the equilibrium of temperature and pressure had been established. This will be the case when the meniscus in the divided stem is moving up and down within the same narrow limits. The stability of the temperature was ensured by a good regulation, and that of the pressure was easily obtained and preserved by paying attention to the oil-trays mentioned in § 2, which immediately betrayed the slightest leakage [1]).

When the above mentioned constant state had set in, some readings of the piezometer and the manometer were alternately made. If they agreed, we proceeded to the next point.

With regard to the regulation of the temperature the measurements took place under the same circumstances as the investigations with the hydrogen thermometer described in Comm. N°. 95^e (Oct. 1906). Besides the resistance-thermometer for regulation and determination of the temperature the thermo-element was also used here by way of control for the determination of the temperature. The indications of the resistance-thermometer, however, proving more reliable than those of the thermo-element, only those of the latter apparatus were used for the calculations. All possible care was always taken that the temperatures at which determinations were made, lay as close as possible to those which have been used for the calibration of the resistance-thermometer to render the corrections small, and the accuracy of the determination of the temperature as great as possible.

The regulation of the pressure took place according to the indication of the metal manometer M of Pl. I, fig. 1. If we passed but slowly from one pressure to the other the thermal process in the reservoir which attended it, was so slight, that the regulation and the measure-

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[1]) Formerly this often required a long and sometimes fruitless search (cf. e.g. comm. N°. 70 p. 8).

ment of the temperature did not experience any perceptible disturbance, on account of which the stability of the bath was the more ensured throughout a whole determination of an isotherm.

§ 8. *Calculation of the observations.*

The calculation is made in the same way as described in Comm. N°. 78 § 8.

For the calculation of the variability of the volume of the piezometer-reservoir U_1 at low temperatures we started from the quadratic formula for k found in Comm. N°. 95^b § 1, so that $k_1 = 23.43 \times 10^{-3}$ and $k_2 = 0.0272 \times 10^{-6}$. No correction for glass-expansion was required for the volume of the glass capillary U_2 nor for that of the steel capillary U_3. For the reduction of the gasvolume in the glass capillary U_2 to 0° we proceeded as follows: the volume was divided into 5 parts U_{2a}, U_{2b}, U_{2c}, U_{2d} and U_{2e}. U_{2a} represents the part in the liquid bath increased by 2 cm. of the capillary above the liquid, where the temperature may still be put equal to that of the bath. U_{2b} U_{2c} and U_{2d} form together the remaining part of the capillary in the cryostat above the bath, $U_{2b} + U_{2c}$ corresponds to the volume u'_2 of § 5 of Comm. N°. 95^e and U_{2d} to u''_2. U_{2e} is the volume of the capillary that is outside the cryostat. For the reduction of the volumes U_{2b}, U_{2c} and U_{2d} we started from the same determinations of the temperature as in Comm. N°. 95^e. As on account of the greater density at lower temperatures the mean temperature found cannot directly be used for the reduction, each of the above mentioned volumes is divided into 3 parts, the temperature of each of these parts is derived, and from this the mean temperature is determined according to the formula $t = \frac{\Sigma \frac{t}{T}}{\Sigma \frac{1}{T}}$ in which T represents the absolute temperature. The coefficients of expansion, which are required for the reduction, were determined by means of the general development into series of Comm. N°. 71 with a slight modification of the coefficients mentioned there. The results obtained in this way do not give an appreciable difference with those which were found when the reductions are made with the approximate results for the determinations of the isotherms obtained in this way.

With regard to the corrections of the temperature of the volumes U_3 and U_4 we proceeded in a way similar to that of Comm. N°. 78. For that of the reservoir at low temperature a somewhat different way

was followed. As practically the temperature for every individual determination of the temperature might be considered as constant (see § 1), a number of parts of isotherms could be immediately obtained for every series separately. As they at the same time refer to about the same densities, an accurate value may be derived for $\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$ from the graphical representation of pv_A on $\frac{1}{v_A}$. The temperatures in the different series not differing more than 0.°2, the results could be reduced to one and the same standard-temperature in this way without the slightest difficulty. As standard-temperatures were assumed the temperatures —103°.57 and —135°.71 of series I, —182°.81 and —195°.27 of series II and —204°.70, —212°.82 and —217°.41 of series III. In the subjoined table the values of $\left(\frac{pv_{A t''} - pv_{A t'}}{t'' - t'}\right)_{v_A}$ are given, which served for the reduction of the remaining determinations of the isotherms to these standard temperatures t_s, which relate to the hydrogen-thermometer at constant volume and 1100 mM. pressure at 0°.

TABLE VII. $H_2 \left(\alpha_p\right)_{t_{s_1}}^{t_{s_2}}$ Series II.

Density.	$\left(\alpha_p\right)_{-182°.81}^{-195°.27}$	$\left(\alpha_p\right)_{-195°.27}^{-204°.83}$	$\left(\alpha_p\right)_{-204°.83}^{-212°.98}$
150	0.004336	0.004406	0.004501
160	0.004390	0.004458	0.004540
170	0.004440	0.004513	0.004588
184	0.004508	0.004599	0.004667

From these mean coefficients values for $\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$ could be derived for the different points of the respective isotherms, which for the isotherm of —212°.82 have been given in Table XI of § 10.

§ 9. *Survey of a determination.*

As an instance of determinations of isotherms at low temperatures we give here one of the measurements from the 3rd series at a density 326 times the normal, in oxygen boiling under strongly reduced pressure.

TABLE VIII. H_2 Series III N° 7. Determination in oxygen at about — 213° C.

Time 3.10—3.20	A	B	C	D	E	F	G	H	K
Piëzometer top	5.8	56.496	— 213°	20°.76	19°.5				
rim	4.8	56.360	— 188°		19°.4	21.6			
division n° 29	7.0	56.864	— 98°		19°.4				
			— 11°						
Manometer						5.0	93.97	19.98	
								20.04	
Piëzometer top	5.9	56.493		20°.76	19°.4				
rim	4.8	56.360				21.6			
					19°.3				
Manometer						5.0	93.97	20.00	
								20.05	
Float									1.3

The columns of the table agree in the main with those of table IX of Comm. N° 78^b. A and B have the same meaning, C denotes the temperature t_1 of the piezometer-reservoir in the bath, and the temperatures t_{2b} t_{2c} and t_{2d} in the order of the parts U_{2a} U_{2b} and U_{2c} (see § 8) of the glass stem in the cryostat above the bath. The temperatures given in this column are to be considered as constant throughout the determination, and have, therefore, been mentioned only once. D gives the temperature t_4 of the waterbath round the stem b_4, E the temperatures t_3', t_3'' and t_3''' of the thermometers placed along the steel capillary. The temperature of the part U_{2e} that projects above the cryostat is put equal to t'_3. The columns F, G and H have the same meaning as in the above mentioned table. In column K the indication of the float in the cryostat has been given. All lengths are in cms.

These readings are corrected in the same way as was followed for table X of Comm. N°. 78^b. These corrected values are given in the following table. The two readings of the piezometer have afterwards been united to a mean after reduction.

TABLE IX. H_2, Series III. Determination at about —213° C. Corrected and recalculated data.

	A	B	C	D	E	F	G	H	K
Manometer mean						115.5	93.97	19.93	
Temperatures t_1, t_4, t_3			—213°	20°.70	18°.6				
t_{2b}			—188°						
t_{2c}			— 98°						
t_{2d}			— 11°						
Piëzometer	28.634	0.135				82.3			
	28.631	0.132							
Surface of the liquid									1.9

The columns from A to H (H included), have the same meaning as those of table X of Comm. N°. 78^b. K denotes the position of the liquid level above the boundary of the piezometer-reservoir and the glass stem, derived from the indications of the float.

From this the following table is obtained, which gives the corrections of volume and pressure required for the calculation of pv_A. It corresponds to table XI of Comm. N°. 78.

The volumes of the parts of the glass capillary with their corrections have been separately given. Moreover the corrections v'_3 and h have been added, the former is a consequence of the packings being pressed down at g_1 and g_2, the latter accounts for the weight of the compressed air in the connecting tube between the manometer and the piezometer. The vertical distance of the levels of the mercury is about 0.5 meters. Instead of the mean coefficient of expansion k, the double term $k_1 + k_2 t$ has been assumed (cf. § 8) for the computation of the correction v_1.

Here we must point out that as standard temperature t_α for the reduction of the parts into which the glass capillary is divided, $+ 20°$ has been assumed, so that the differences $t_\alpha - t_2$ are not very small here. The method of interpolation applied in Comm. N°. 78 for small values of $t_\alpha - t_2$ will be used as soon as we have tables for $d_{\alpha p_2}$ at our disposal. The values have been directly determined here by calculation.

TABLE X, H_2. Series III. Corrections and final result.

$U_4 =$	4.4904 cm³.	$p_m =$	61.004 atm.
$w_4 =$	0.0003 »	$H_p =$	0.434 »
$w'_4 =$	0.0014 »	$h =$	— 0.004 »
$u_4 =$	— 0.0104 »		
$u_3 =$	0.0018 »	$u'_3 =$	— 0.0005 cm³.
$U_{2a} =$	0.0018 »	$u_{2a} =$	0.0059 »
$U_{2b} =$	0.0020 »	$u_{2b} =$	0.0049 »
$U_{2c} =$	0.0025 »	$u_{2c} =$	0.0024 »
$U_{2d} =$	0.0129 »	$u_{2d} =$	0.0015 »
$U_{2e} =$	0.0190 »	$u_{2e} =$	0.0001 »
$w_1 =$	— 0.0239 »	$w'_1 =$	0.0012 »
$(pv_A)_{t_1} = 0.18863$		$t_1 =$	— 212°.82
$(pv_A)_{-212°.82} = 0.18863$		for $p =$	61.434 atms.

The total value of the correction of the stem appears to be very small, so that we might apply the law of GAY—LUSSAC down to —217° without introducing appreciable errors.

§ 10. *Values of pv_A.*

The values of pv_A obtained in this way for the different determinations have been represented for the isotherm of —212°.82 in the following table. The values in the last columm refer to the reduction to the standard-temperature t_s (cf. the conclusion of § 8).

The values of this table have been obtained, as appears from table IX, by calculation with the mean values of the separate readings. The deviations in these separate readings which may be due both to oscillations of the pressure and the temperature and to errors in the readings themselves, amount nowhere to more than $\frac{1}{2000}$.

The result found for about the same point at the beginning and at the end of one determination of an isotherm are in very good accordance, as moreover is to be seen by comparing observation

TABLE XI. H_2. Results for the isotherm of —212°.82.

N°.		t_1	p	pv_A	d_A	$\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$
Series II	17	— 212°.98	30.591	0.19406	157.64	0.00458
	18		35.426	0.19134	185.15	0.00473
	19		33.071	0.19264	171.68	0.00465
	20		30.554	0.19405	157.46	0.00458
Series III	6	— 212°.82	51.632	0.18767	275.12	
	7		61.434	0.18863	325.68	

N°. 17 and N°. 20 of table XI. The results are reduced to the same standard-temperature by means of the values of $\left[\frac{d(pv_A)}{dt}\right]_{t_1 v_A}$ given in the last column.

In table XII the results obtained in this way are also given for the remaining isotherms. Those belonging to series I are less certain and will be repeated.

The results obtained at the beginning and at the end of a determination of an isotherm at about the same density have been united to a mean.

For every temperature we have added to the results of the determinations of isotherms those of the readings of the hydrogen-thermometer to which the former are in direct relation.

The numbers do not agree with those of the preceding table, because some determinations have been united to a mean, for which reason they are indicated by ( ).

The points of the hydrogen-thermometer have been obtained in the following way. From SCHALKWIJK's determinations of isotherms follows for 20° C.

$$pv_A = 1.07258 + 0.000667\, d_A + 0.00000099\, d_A^2.$$

If we suppose the mean pressure-coefficient from 0° to 20° not to deviate appreciably from the value 0.0036627 between 0° and 100°, which is permissible on account of the insignificant deviations of the indications of the hydrogen-thermometer of constant volume from the absolute scale, it follows from this that:

$$(pv_A)_{0°,\ 1100\ mm.} = 1.000275.$$

The value given in Comm. N°. 60 having been taken for the pressure-coefficient of hydrogen for the calculation of the hydrogen

TABLE XII, H_2. Values for $(pv_A)_{t_s}$.

N°.		t_s	p	pv_A	d_A
H_2 therm.	(1)	— 103°.57	0.896	0.62082	1.444
Series I	(2)		32.985	0.63467	51.971
	(3)		39.659	0.63765	62.193
	(4)		49.897	0.64274	77.632
H_2 therm.	(1)	— 135°.71	0.727	0.50307	1.445
Series I	(2)		28.592	0.51064	55.991
	(3)		33 437	0.51258	65 231
H_2 therm.	(1)	— 182°.81	0.479	0.33051	1.448
Series II	(2)		46.572	0.32700	142.42
	(3)		55.293	0.32822	168.46
H_2 therm.	(1)	— 195°.27	0.413	0 28486	1.449
Series II	(2)		40.599	0.27367	148.35
	(3)		45.484	0 27337	166.36
	(4)		49.998	0.27343	182.85
H_2 therm.	(1)	— 204°.70	0 363	0.25031	1.449
Series II	(2)		35.487	0.23189	153 03
	(3)		38.640	0.23097	167.30
	(4)		42.438	0.23010	184.43
Series III	(5)		61.917	0.23009	269.10
H_2 therm.	(1)	— 212°.82	0 320	0.22056	1.450
Series II	(2)		30.689	0.19480	157.64
	(3)		33.200	0.19339	171.68
	(4)		35.566	0.19210	185.15
Series III	(5)		51.632	0.18767	275.12
	(6)		61.434	0.18863	325 68
H_2 therm.	(1)	— 217°.41	0 295	0 20375	1.450
Series III	(2)		46.419	0.16381	283.81
	(3)		52.898	0.16336	323 80
	(4)		58.971	0.16424	359.04

thermometer-temperatures, the value of pv_A at t_s now follows from the formula

$$(pv_A)_{t_s} = (pv_A)_s(1 + 0.0036627\, t_s).$$

§ 11. *Probable error of a determination.*

The mean error in the calibration of the large volume of the piezometer may be estimated at $\pm \frac{1}{4000}$. As to the volume into which the gas is compressed during the measurements, the greater density of the gas in the reservoir at low temperatures may be allowed for by reckoning only with $\frac{1}{3}$ of the amount of the volumes at the temperature of the room. The errors in these volumes being predominant with respect to those in the volume of the piezometer reservoir, the mean error for measurements below —180° with piezometers of 5 c.M³ may be put equal to $\pm \frac{1}{3000}$ of the compressed volume in accordance with the degree of accuracy as was calculated in Comm. N°. 69, where for measurements at the ordinary temperature the mean error is estimated at $\pm \frac{1}{1000}$ for piezometers of 5 c.M³. For —100° the mean error will be $\pm \frac{1}{2000}$.

The mean error of the determinations of the normal volume is $\pm \frac{1}{3000}$, that of the measurements of the pressure may also be estimated at $\pm \frac{1}{3000}$.

In the determination of the temperature there is no appreciable error. The observations made for one point show that the mean error due to variations of temperature and faulty readings of the position of the mercury in the stem, may be put smaller than $\pm \frac{1}{5000}$.

The mean error of the determination of temperature in the stem remains below $\pm \frac{1}{6000}$.

The mean error caused by all these sources of errors together amounts to $\pm \frac{1}{1500}$ for piezometers of 5 c.M.³ and not very low temperature, to $\pm \frac{1}{1700}$ for larger piezometers and very low tempe-

ure. The different points on one and the same isotherm must show smaller discrepancies inter se than corresponds with the said mean error. The mean error namely, for a determination, apart from the errors in the determination of the normal volume and the calibration of the large volume is $\pm$ from $\frac{1}{2000}$ to $\pm$ $\frac{1}{2400}$.

All this does not apply to the isotherms of $-103°.57$ and $-135°.71$. These belonging to series I are the earliest determinations and for different reasons less accurate than the later ones.

§ 12. *Provisional individual virial coefficients.*

If the temperatures had not been given as readings on the hydrogen-thermometer of constant volume at 1100 mm. pressure, but on the absolute scale, the coefficients A_A, B_A etc. calculated from the equation

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2_A} + \frac{D_A}{v^4_A} + \frac{E_A}{v^6_A} + \frac{F_A}{v^8_A} \quad . \quad . \quad . \quad (1)$$

with the values of pv_A from table XII, could be immediately compared with those derived in Comm. N°. 71 [1]). However, this is not the case, because the latter relate to the absolute scale of temperature. From the outset it has been our purpose to derive the correction of the hydrogen scale on the absolute scale experimentally from our measurements themselves. This might be attained by first neglecting the correction, and by calculating provisional values A'_A, B'_A, C'_A etc. for each of the isotherms, which serve then for finding provisional corrections for the hydrogen-thermometer; after this the calculation is repeated with the corrected temperatures, etc., till further repetition would not bring about any change. A similar treatment has been applied for the determination of the corrections of the readings of the hydrogen-thermometer to the absolute scale, where we purposed to draw through the observations for every isotherm a curve, which does not only correspond as closely as possible to the observations, but also to the general equation of state. In this §

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[1]) We must call attention to the fact that in the calculations of Comm. N°. 71 we began by taking 273°.04 by first approximation for the absolute zero-point; we should find the correction to this from the results of the calculations of isotherms, and then proceed to a second approximation. We have still retained 273°.04 in VI. 1 Suppl. N°. 8 and in VI. 2 Comm. N°. 92. Since then, however, a set of coefficients VII. 1, which will be published in the following communication, have been calculated with the further approximation for the absolute temperature, viz. the more accurate value 273°.09, and corrections have, moreover, been applied in critical quantities etc.

the method of least squares has been applied directly to the individual isotherms, in order to obtain a formula which represents the observations as accurately as possible.

The number of points on each isotherm not being large enough for all six coefficients to be determined at once, definite values were assumed for the last three values. F_A was put $= 0$, and values were calculated for D_A and E_A from the sets of coefficients VII.1 [1]), which was chosen instead of V of Comm. N°. 71. This assumption means, that a definite course was prescribed for the isotherms at higher densities, which corresponds as closely as possible to the law of the corresponding states. The results of these calculations are laid down in the subjoined table. D_A and E_A are the values assumed for the calculation according to the above.

TABLE XIII. H_2. Provisional virial coefficients.

t_3	A'_A	$10^3.B'_A$	$10^6.C'_A$	$10^{12}.D'_A$	$10^{18}.E'_A$
— 103°.57	0.62048	0.24271	0.5584	0.9113	— 0.648
— 135°.71	[0.50303	0.03234	1.7974	0.7028	— 0.408]
— 182°.81	0.33063	— 0.08384	0.4021	0.3809	— 0.088
— 195°.27	0.28503	— 0.13051	0.3565	0.2892	— 0.016
— 204°.70	0.25058	— 0.18030	0.3710	0.2166	0.031
— 212°.82	0.22090	— 0.22433	0.3668	0.1514	0.066
— 217°.41	0.20410	— 0.25013	0.3715	0.1122	0.082

It appears from the table, that the coefficients of the same column vary regularly with the temperature, except for — 135°.71, for which we may account by taking into consideration that the two piezometer-determinations which had to be used for the calculation, lie so close together, that a slight difference in their relative situation already produces a large difference in B'_A and C'_A.

By the aid of the coefficients the values of pv_A were determined anew according to formula (1). The divergencies for every isotherm between the assumed values of pv_A, W_i and the R_{oi} calculated with A'_A, B'_A and C'_A ($pv_A = 1$ for 0° and 760 mm.), where i indicates the number of that observation in table XII, have been represented in the subjoined table.

[1]) For the calculation of D_A and E_A the uncorrected reading of the hydrogen thermometer was used (see preceding note).

TABLE XIV H_2. Deviation from formula (1).

	$10^5\,(W_i - R_{oi})$						in % of R_{oi}					
t_s	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$
—103°.57	—1	+7	—9	+3			0.001	0.011	0.015	0.005		
—135°.71												
—182°.81												
—195°.27	+1	+1	—4	+2			0.004	0.004	0.014	0.007		
—204°.70	—1	+9	0	—9	+1		0.004	0.036	0.000	0.036	0.004	
—212°.82	—2	+5	+6	—2	—17	+10	0.007	0.022	0.027	0.009	0.077	0.045
—217°.41	0	0	—3	+2			0.001	0.000	0.014	0.010		

The isotherm of — 212.°82 is best adapted to give an idea of the accuracy of the mutual agreement on account of its larger number of points. The agreement proves very satisfactory. The upper limit of the mean error may be put at $\pm\frac{1}{2000}$.

§ 13. *Minima of pv.*

By means of the coefficients of table XIII the following minima of the *pv*-curves were derived from the data of table XII.

TABLE XV. H_2. Minima of $p\,v_A$.

t_s	$p\,v_A$	d_A	p	$W - R_0$
— 182°.81	0.32630	102.24	33.36	— 0.08
— 195°.27	0.27338	174.45	47.69	+ 0.50
— 204°.70	0.22935	227.17	52.10	— 0.75
— 212°.82	0.18780	285.55	53.63	+ 0.26
— 217°.41	0.16335	315.72	51.57	+ 0.08

By means of the method of least squares the coefficients of a parabola

$$p = P_0 + P_1\,(pv_A) + P_2\,(pv_A)^2$$

have been calculated from these data [1]). They are:

[1]) It is to be remarked that the less certain isotherms of — 104° and — 136° are not used in this deduction.

H KAMERLINGH ONNES and C. BRAAK. Isotherms of di-atomic gases and their binary mixtures. VI. Isotherms of hydrogen between — 104° C. and 217° C.

Plate I.

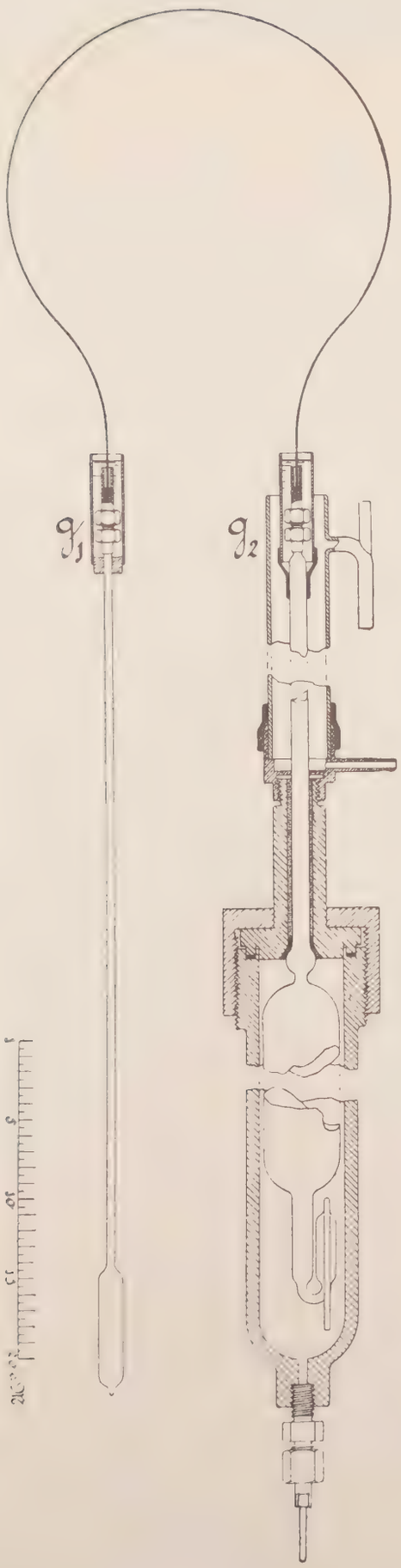


Fig. 2.

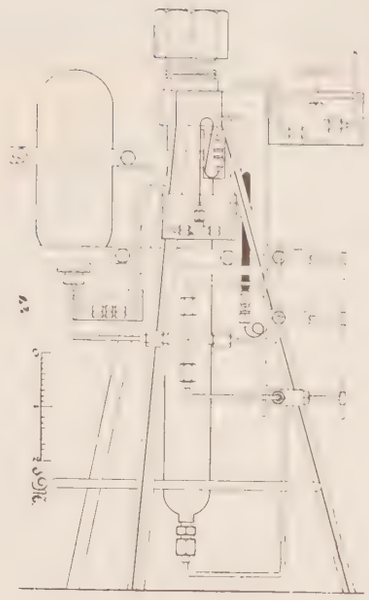


Fig. 3.

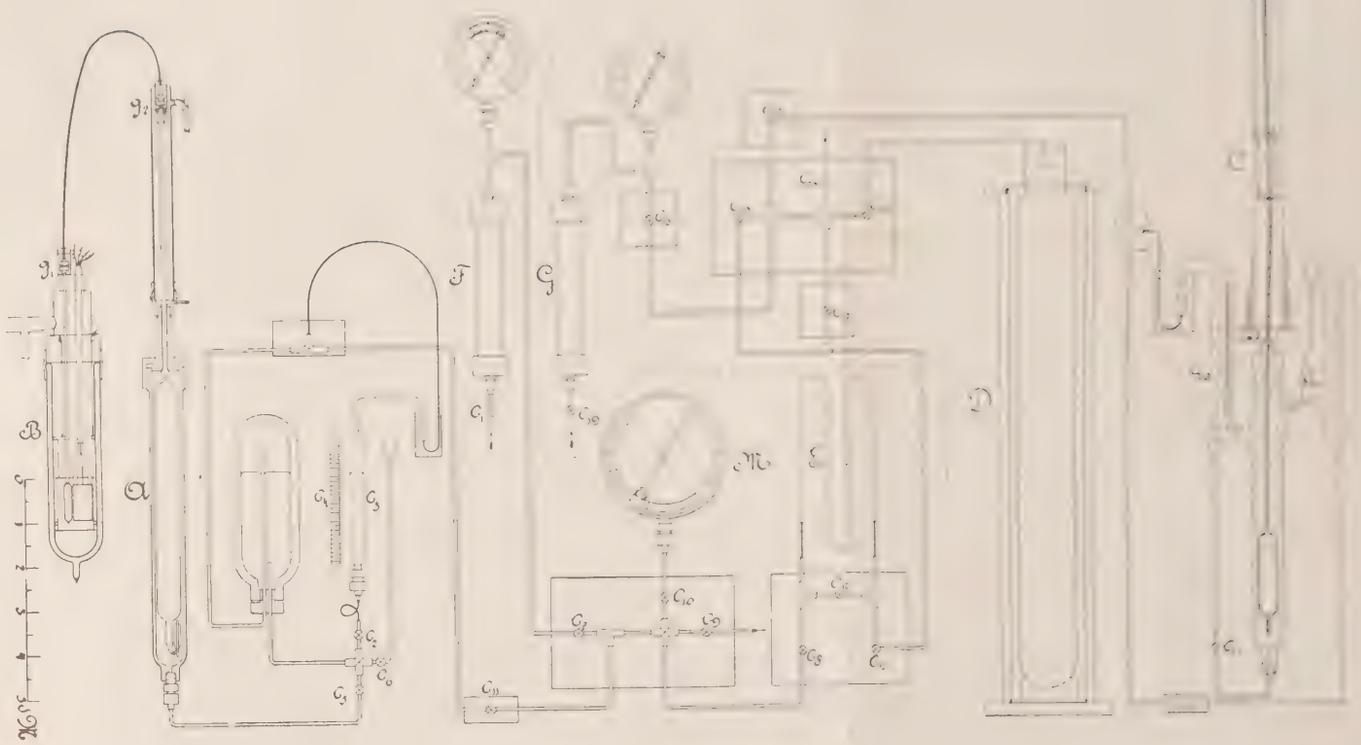


Fig. 1.

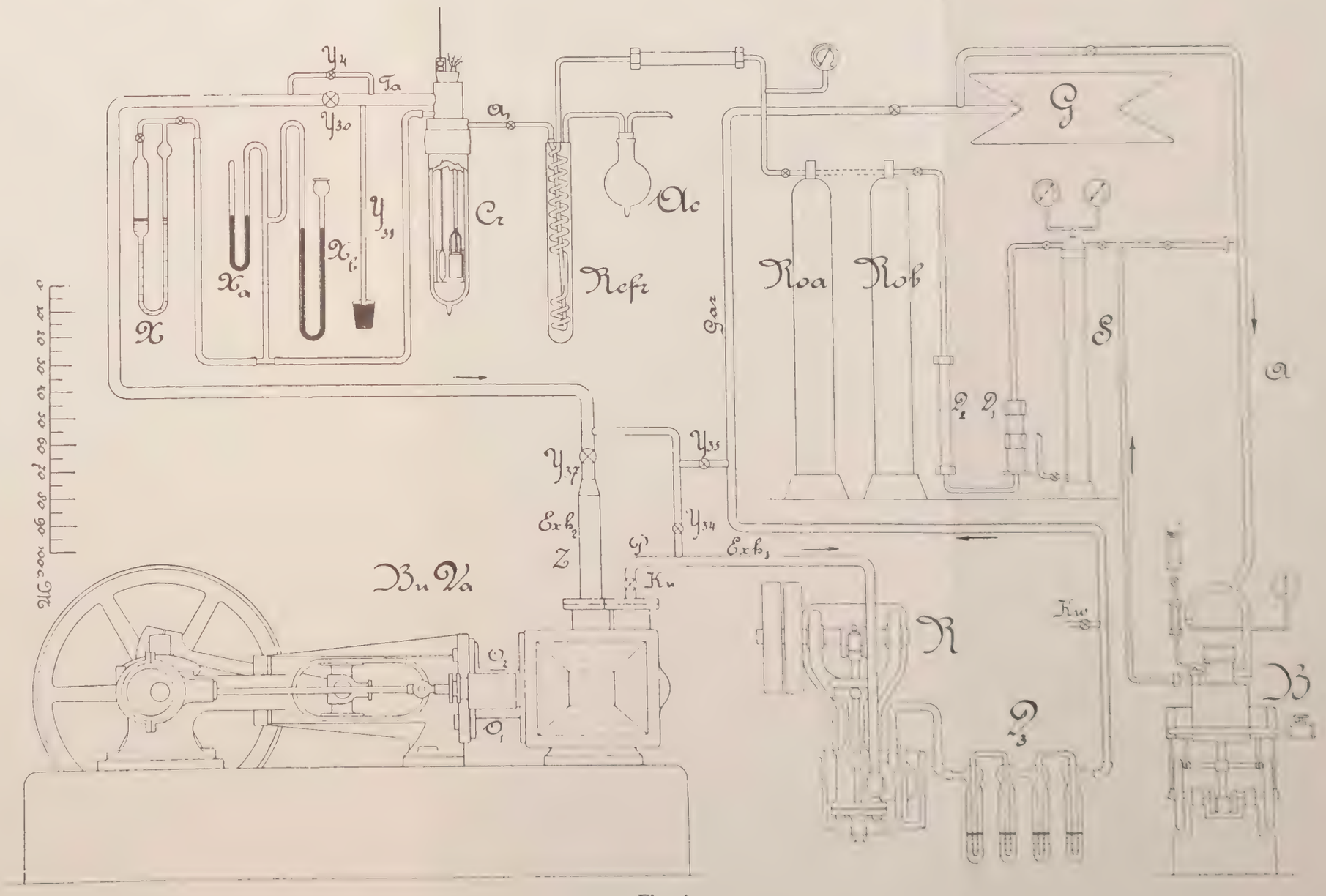
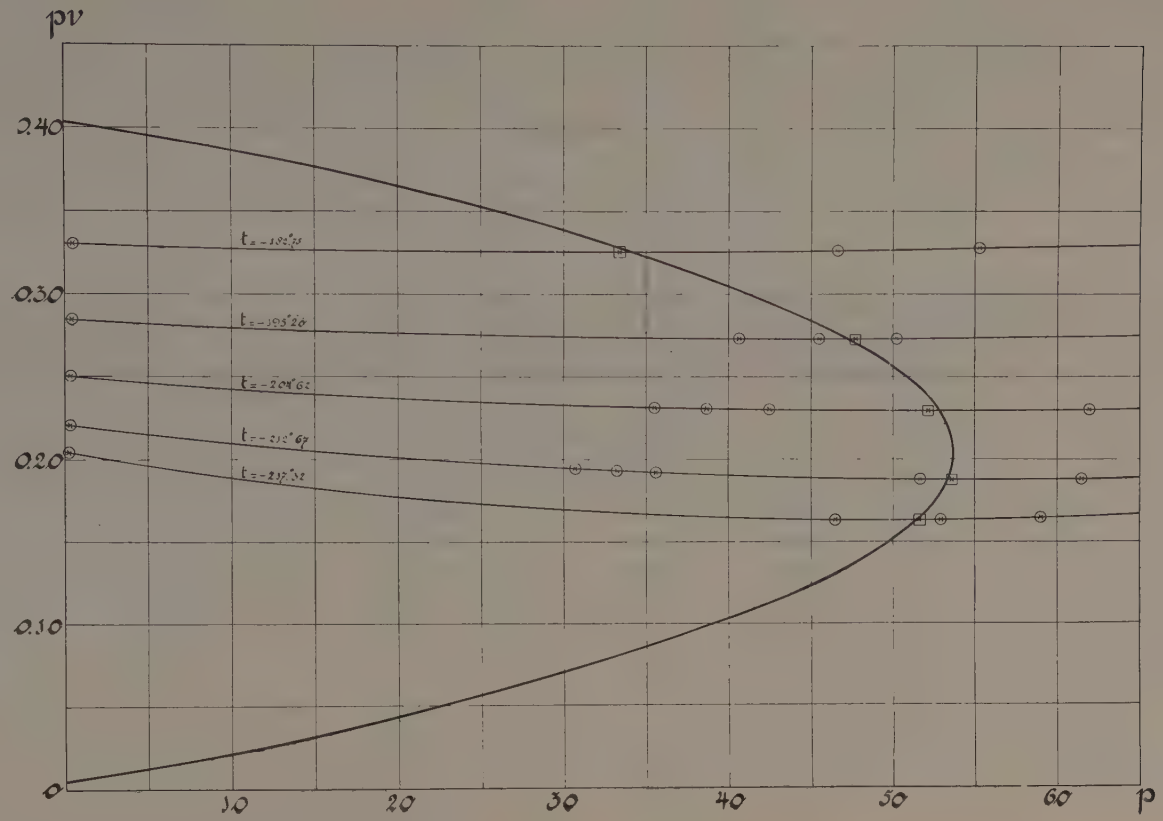


Fig. 4.

H. KAMERLINGH ONNES and C. BRAAK. Isotherms of di-atomic gases and their binary mixtures.
VI. Isotherms of hydrogen between −104° C. and −217° C.

Plate II.



$$P_0 = -2.623$$
$$P_1 = 552.610$$
$$P_2 = -1354.86.$$

The differences $W - R_0$ between the given values of p and those calculated with these coefficients have been represented in the last column of table XV. They amount to little more than $\frac{1}{2}$ atmosphere. The results given in the table have been reproduced in a diagram on Pl. II [1]); the curve traced there is the calculated parabola.

It follows further from the values of the coefficients, that the parabola cuts the ordinate $p = 0$ in two points, where pv_A is respectively 0.00480 and 0.40307, from which follows with the formula [2])

$$(pv_A)_T = 0.99939 \{1 + 0.0036618 (T - 273°.09)\}$$

for the corresponding temperatures measured on the absolute scale,

$$T_1 = 1°.3 \qquad T_2 = 110°.2.$$

The top of the parabola lies at a pressure of 53.73 atms. the value of pv_A is here 0.20394, from which follows, in connection with the value of $\left(\frac{d(pv_A)}{dt}\right)_{p=53.73}$ determined from the isotherms, viz. 0.0053, for the absolute temperature of the isotherm which passes through the top that

$$T = 63°.5.$$ [3])

Physics. — "*On the measurement of very low temperatures. XIV. Reduction of the readings of the hydrogen thermometer of constant volume to the absolute scale.*" By Prof. H. KAMERLINGH ONNES and C. BRAAK. Communication N°. 97b from the Physical Laboratory at Leiden.

(Communicated in the meeting of Jan. 26, 1907).

§ 1. *Introduction.*

As it is till now difficult to obtain pure helium, and very easy to obtain pure hydrogen (c.f. Comm. N°. 94f, June 1906), the scale of the normal hydrogen thermometer (that with constant volume under a pressure of 1000 m.M. of mercury at 0°) is for the

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1) The temperatures have been given in absolute degrees below zero. The temperatures noted down on the plate undergo slight alterations on account of a more accurate calculation of the corrections to the absolute scale. They become −103°.54, −135°.67, −182°.75, −195°.20, −204°.62, −212°.73 and −217°.32.

2) This value of A_{AO} has been calculated from SCHALKWIJK's determinations of isotherms (cf. the conclusion of § 10).

3) In this the corrections to the absolute scale have been taken into account.

present, just as when it (1896) was first mentioned as the basis of the measurement of low temperatures at Leiden in the first communication (N°. 27) on this subject, still the most suitable temperature-scale to determine low temperatures down to —259° unequivocally with numerical values, which come nearer to the absolute scale than those on any other scale. It is therefore of great importance to know the corrections with which we pass from the normal hydrogen-scale to the absolute one.

As is known they may be calculated for a certain range of temperatures, when the equation of state for this region of temperature has been determined at about normal density. Up to now we had to be satisfied for that calculation for the hydrogen thermometer below 0° with equations of state of hydrogen obtained in a theoretical way. BERTHELOT [1]) derives them by means of the law of the corresponding states from experimentally determined data of other substances in the same region of reduced temperature. CALLENDAR [2]) modifies VAN DER WAALS' equation of state so as to render it adapted to represent the results of the experiments of JOULE—KELVIN for air and nitrogen as well as those for hydrogen between 0° and 100°, and supposes that a same form of equation holds also for hydrogen outside this region. Chiefly this comes to the same thing as the application of the law of the corresponding states, albeit to a limited group of substances. Though such theoretic corrections as have been given by BERTHELOT and CALLENDAR are a welcome expedient to help us in default of other data [3]), yet an experimental determination of these corrections remains necessary.

We have obtained them in this research by using the isotherms of hydrogen between —104° C. and —217° C. given in Comm. N°. 97*a*.

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[1]) Sur les thermomètres à gaz, Travaux et Mémoires du Bureau International, T. XIII.

[2]) Phil. Mag. [6] 5, 1903.

[3]) WROBLEWSKI's determinations of isotherms at the boiling point of ethylene and oxygen are not accurate enough for this purpose. In the results found for the last temperature this is immediately apparent from the irregular situation of the points on the isotherm. The values obtained at the boiling-point of ethylene give more harmonious results. And yet a correction on the absolute scale would follow from them which has the wrong sign, viz. — 0°.07.

At the temperature of liquid air TRAVERS has determined the difference of the hydrogen thermometer of constant volume and constant pressure, from which we may also derive the corrections to the absolute scale for these temperatures. It is obvious that this derivation cannot be very trustworthy.

Further it is now possible (see § 1 of Comm. N°. 97*a*) to derive data on the expansion of hydrogen at low temperatures from the determinations of WITKOWSKI; they will be discussed in a following communication.

For the calculation of these corrections at a definite temperature we might start from the individual virial coefficients in the development into series of the equation of state (cf. Comm. N°. 71, 1901), which we have derived in § 12 of Communication N°. 97a. The results obtained in this way show really a regular course[1]), in spite of the small number of points on the isotherms.

However, we wished first to adjust the results of the separate isotherms by general formulae of temperature. Both in this case and in general it is very difficult to succeed in this by application of one of the equations of state drawn up in a finite form. Very suitable for such a purpose is the general development into series (or more strictly speaking, development into a polynomial), which has already been mentioned frequently. We chose for this the form VII. 1 (cf. the footnote to § 12 of Comm. N°. 97a). The adjustment takes place by calculating for every isotherm modifications in B and C, ΔB and ΔC, which we call individual ΔB and ΔC, with an approximate value of the correction to the absolute scale, by then representing the values of ΔC by a general formula of the temperature, and by computing new values for ΔB by successive approximation in such a way that the value for the correction on the absolute scale corresponds to the assumed value of T. Finally also the values of ΔB were represented by a general formula of the temperature.

If we put the new values of B and C obtained by the aid of these corrections, which *special* values we denote by VII. H_2. 1 in the polynomial of state, then this represents at the same time the determinations of isotherms of Comm. N°. 70 at 20° very satisfactorily, and those of Comm. N°. 78 at 0° and 20° by approximation.

By means of these general expressions the reductions on the absolute scale have been carried out.

If B and C are known there is another way to derive the absolute temperature from the observations with the hydrogen thermometer, than by applying the corrections which lead from the hydrogen scale to the absolute temperature scale. In the calculation of the temperature from the observations we may namely take at once into account, that the gas in the thermometer does not follow the law of BOYLE-CHARLES, but that pressure and volume are connected in the way, as is indicated by the development into series with the corrected values of B and C. The formula which may serve for this purpose, is given in § 5.

[1]) Only the isotherm of — 135°.71 gives a deviating result. (See the conclusion of § 12 of the preceding communication).

§ 2. *Reduction of the readings of the hydrogen thermometer of constant volume to the absolute scale.*

If v is the volume of the gas in the thermometer, expressed in the theoretical normal volume, p the pressure in atmospheres, T the absolute temperature, the equation of state for the thermometer gas may be written in the form:

$$pv = A_T\left(1 + \frac{B'_T}{v} + \frac{C'_T}{v^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Further we put:

t the temperature on the scale of the hydrogen thermometer of constant volume

and

$$T - T_{0^\circ\,\mathrm{C.}} = \theta.$$

t is determined by

$$t = \frac{(pv)_T - (pv)_0}{(pv)_0\,\alpha_p},$$

where α_p represents the mean pressure-coefficient between 0° and 100° for the thermometer with the specific volume v. This is given by $\dfrac{(pv)_{100} - (pv)_0}{100\,(pv)_0}$.

If we represent the correction on the absolute scale by:

$$\Delta t = \theta - t,$$

we may write for this:

$$\Delta t = \frac{(T-T_0)\left(\frac{T_{100}B'_{100} - T_0B'_0}{100\,v} + \frac{T_{100}C'_{100} - T_0C'_0}{100\,v^2}\right) - \left(\frac{TB'_T - T_0B'_0}{v} + \frac{TC'_T - T_0C'_0}{v^2}\right)}{1 + \frac{T_{100}B'_{100} - T_0B'_0}{100\,v} + \frac{T_{100}C'_{100} - T_0C'_0}{100\,v^2}} \quad (3)$$

In agreement with what may be derived from the mean equation of state VII. 1, it appears from our determinations, that the influence of C'_T is very slight, and down to — 217° does not amount to more than 0°.0003, so that it has not to be taken into account. Therefore in what follows will be put $C'_T = 0$, as is also done by BERTHELOT but without proof.

For the absolute zero point the value 273°.09 [1]) is assumed, from

[1]) From AMAGAT's experiments with the development into series of Comm N°. 71 (cf. the note to § 12 of Comm. N°. 97^a) 1.26×10^{-5} was found for the difference between the pressure-coefficients of nitrogen at 1000 mm. pressure and 0 mm. pressure, from which follows with CHAPPUIS' pressure-coefficient for 1000 mM., i. e. 0.0036744 the value 0.0036618 for the limiting value at 0 mM. pressure, corresponding to the absolute zero point — 273°.09. In the same way hydrogen gives for the difference of the pressure-coefficients at 1090 mM. and 0 mM. 2.1×10^{-6}, which with the pressure-coefficient 0.0036629 given in Comm. N°. 60 (see XV) gives

which follows $A_T = 0.0036618\, T$, $T_{0°C.} = 273°.09$ and $T_{100°C.} = 373°.09$.

For the reduction of the data given in Comm. N°. 97^a to the theoretical normal volume the value $\frac{v_A}{v} = 0.99939$ was taken, borrowed from the determinations of isotherms of Comm. N°. 70 (SCHALKWIJK).

The values of B'_0 and B'_{100} have been derived from the same determinations of isotherms [1]) by the aid of the pressure-coefficient 0.0036629 (see XV at the end of this Communication), neglecting the correction to the absolute scale for 20°. These values are: [2])

$$B'_0 = 0.000607 \qquad B'_{100} = 0.000664$$

The values of B'_T were found from the VII. H_2. 1 already more fully discussed in § 1, which gives in a reduced form [3])

$$10^8\, \mathfrak{P} = +\, 173.247\, t - 462.956 - 706.416\, \frac{1}{t} + 384.2458\, \frac{1}{t^3} - 4.2530\, \frac{1}{t^5}$$

whereas VII. 1 gives:

$$10^8\, \mathfrak{V} = 157.9500\, t - 305.7713 - 231.8247\, \frac{1}{t} - 97.5686\, \frac{1}{t^3} - 4.2530\, \frac{1}{t^5}$$

From this the values of B'_T have been calculated for the standard temperatures of the isotherms.

The subjoined table contains in the first column these standard temperatures t_s measured on the scale of *our* hydrogen thermometer,[4])

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the limiting value 0.0036608. The same value as was found above from nitrogen, was derived by BERTHELOT (loc. cit.) from CHAPPUIS' results for nitrogen and those for hydrogen obtained with a thermometer-reservoir of hard glass. In the same paper he derives the value 273°.08 for the absolute zero-point for the case that also the less concordant results found by CHAPPUIS for hydrogen with a platinum-thermometer are taken into account. Afterwards (see Zeitschrift für Elektrochemie N°. 34, 1904) the first mentioned value 273°.09 is again found by taking the mean of the above values for nitrogen and hydrogen, and those which may be derived by means of the experiments of KELVIN and JOULE.

[1]) Compare the conclusion of § 10 of Comm. N°. 97^a.

[2]) The values found by CHAPPUIS are resp. 0.000579 and 0.000606.
Those of WITKOWSKI are 0.000616 and 0.000688.
Those derived in Comm. N°. 71 from the observations of AMAGAT are 0.000669 and 0.000774.

[3]) According to DEWAR, $p_K = 15$ atms. and $T_K = 29°$ are used for the calculation, which also served for the derivation of VII. 1.

Further have been put $A_{AO} = 0.99939$ and $A_A = A_{AO}\,(1 + 0.0036618\, t)$.

[4]) The slight differences with the value of table XII of Comm. N°. 97^a are due to a correction (see XV) in consequence of the application of the improved pressure-coefficient 0.0036629 and the influence of the dead space on the determinations of the temperature, which will be more fully discussed in the last part of this communication.

in the second column the same temperatures measured on the absolute scale. The two following columns contain the corresponding values of the special B'_T and of the corrections to the absolute scale Δt_s calculated according to formula (2) for a hydrogen-thermometer of constant volume with 1090 mm. zero-point-pressure. The last column gives the corrections for the *normal* hydrogen-thermometer.

The values for $-103°.56$ and $-135°.70$ are less certain than the others (compare § 10 and § 11 of the preceding communication).

TABLE XVI. H_2. Corrections to the absolute scale.

t_s	θ	$B'_T.10^3$	Δt_s	Δt
$-103°.56$	$-103°.54$	$+0.3892$	$0°.0214$	$0°.0196$
$-135°.70$	$-135°.67$	$+0.2368$	$0°.0316$	$0°.0290$
$-182°.80$	$-182°.75$	-0.2327	$0°.0530$	$0°.0486$
$-195°.26$	$-195°.20$	-0.4734	$0°.0611$	$0°.0561$
$-204°.69$	$-204°.62$	-0.7244	$0°.0683$	$0°.0627$
$-212°.81$[1]	$-212°.73$	-1.0112	$0°.0752$	$0°.0690$
$-217°.40$	$-217°.32$	-1.2167	$0°.0796$	$0°.0730$

With very close approximation the results of the last column may be represented by the formula:

$$\Delta t = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + d\left(\frac{t}{100}\right)^4 \quad . \quad . \quad . \quad (4)$$

where:

$$a = -0.0143307$$
$$b = +0.0066906$$
$$c = +0.0049175$$
$$d = +0.0027197$$

The greatest deviation is three units of the last decimal.

The formula gives the value $\Delta t = 0$, both for $t = +100°$ and for $t = 0°$, while $\Delta t = +0°.14$ would follow from it for $t = -273°$.

§ 3. *Accuracy of the corrections.*

The influences which may cause errors in the corrections, are of two kinds.

1. Errors in the values of B'_T.

2. Errors in the data which have been used in the further derivation.

[1]) The difference with Comm. N°. 97*a* remaining after the correction of the preceding note is the consequence of an improvement applied in the calculation.

The latter may be reduced to the error in B'_0 and the difference of the pressure-coefficients used for the density $= 0$ and that at 0° and 1090 mM. If for the mean error in B'_0 we compare the values of B'_0 which may be derived from the data of Comm. N°s. 70 and 78 and from those of CHAPPUIS, a mean error of $\pm$ 0.000034 (about agreeing with the error per cent derived for the pv in § 11 of Comm. N°. 97[a]) follows from their deviations inter se, which corresponds with a mean error of $\pm$ 0°.008 at $-$ 100° and of $\pm$ 0°.003 at $-$ 200° for Δt.

We may further assume that the mean error in the pressure-coefficients 0.0036618 and 0.0036629 amounts to one unit of the last decimal for the first and to two units for the second, which corresponds with a mean error in Δt of $\pm$ 0°.003 and $\pm$ 0°.006 at $-$ 100° and of $\pm$ 0°.005 and $\pm$ 0°.011 at $-$ 200°.

If we further put the mean error in B'_T equal to that of B'_0, a mean error in Δt corresponds to this of $\pm$ 0°.006 at $-$ 100° and of $\pm$ 0°.002 at $-$ 200°.

The total mean error in consequence of all these mean errors together will amount to $\pm$0°.012 for $-$100° and $\pm$0°.013 for $-$200°.

§ 4. *Comparison of the results with those which have been theoretically derived.*

Table XVII contains the corrections concerning the normal hydrogen

TABLE XVII. H_2. Corrections to the absolute scale.

t	Δt		t	Δt		
	experimental values	according to VII. 1		according to Callendar	according to Berthelot	from experimental values
— 103°.56	0°.0196	0°.0017	— 10°	0°.00021		0°.0015
— 135°.70	0°.0290	0°.0032	— 20°	0°.00048		0°.0031
— 182°.80	0°.0486	0°.0082	— 50°	0°.00164		0°.0082
— 195°.26	0°.0561	0°.0108	— 100°	0°.0054	0°.008	0°.0187
— 204°.69	0°.0627	0°.0136	— 150°	0°.0132		0°.0337
— 212°.81	0°.0690	0°.0168	— 200°	0°.0311	0°.06	0°.0593
— 217°.40	0°.0730	0°.0192	— 240°		0°.18	
240°		0°.0470	— 250°	0°.1005		
250°		0°.0925				

thermometer. Besides the above mentioned values of Δt, which were directly found from the observation it contains the corrections determined according to the serial formula VII. 1 and those calculated by CALLENDAR and BERTHELOT. Moreover in the last column the corrections, which may be calculated from the experimental values adjusted with VII. H_2 according to formula (4) are given for a comparison.

Besides the corrections derived from this investigation for the zero-point-pressure of 1000 m.M., also the values found by BERTHELOT and CALLENDAR are represented on the plate. The three curves have been indicated by I, II and III in the above mentioned order. Also II and III refer to a zero-point-pressure of 1000 m.M.

The values derived by CALLENDAR and BERTHELOT by means of the law of the corresponding states appear to deviate systematically from the experimental ones. With regard to the corrections according to VII. 1., in the derivation of which formula agreement in the region of the equation of state (between 0° and —217° for hydrogen) treated here, was not aimed at, we may observe that a modification is required for VII. 1 to give as good an agreement as possible also in this region. In the first place this agreement would require that for the calculation of VII. 1 those values were assumed for the critical quantities of H_2 which follow from the data of Comm. N°. 97^a. They are $p_k = 15$ atms. and $T_k = 43°$. This value of T_k would considerably increase the corrections given in table XVII according to VII. 1.

§ 5. *Formula to derive the temperature directly from the observations with the gas thermometer of constant volume.*

We suppose that the correction for the difference in pressure at the mercury meniscus and the thermometer-reservoir in consequence of the weight of the thermometer-gas is applied to H_T, and that it is so small that it may be neglected for the small volumes.

The fundamental formula for the reduction is [1]):

$$pv = A_T \left(1 + \frac{B_T}{v} + \frac{C_T}{v^2}\right)$$

which may also be written in the form:

$$pv = A_T \left(1 + B_T^{(p)}\, p + C_T^{(p)}\, p^2\right) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We start from this latter formula. The equation for the gas-thermometer (cf. formula (1) of § 5 of Comm. N°. 95^c) becomes now:

[1]) Here v is expressed in the theoretical normal volume and hence $A_T = 1 + 0.0036618\, t$. We call the value for 0° C., at which $t = 0$, A_{T_0}. It is 1.

$$H_T\left[\frac{V_0(1+k_1 t+k_2 t^2)+\beta_1+u_1}{A_T(1+B_T^{(p)} H_T+C_T^{(p)} H_T^2)}+\frac{u_2'}{A_{t_2'}(1+B_{t_2'}^{(p)} H_T^2)}+\right.$$

$$\left.+\frac{u_2''}{A_{t_2''}(1+B_{t_2''}^{(p)} H_T)}+\frac{u_3}{A_{t_3}(1+B_{t_3}^{(p)} H_T)}+\frac{u_4}{A_{t_4}(1+B_{t_4}^{(p)} H_T)}\right]=$$

$$=H_0\left[\frac{V_0+\beta_2+u_1+u_2'+u_2''+u_2'''}{A_{T_0}(1+B_{T_0}^{(p)} H_0+C_{T_0}^{(p)} H_0^2)}+\frac{u}{A_{15}(1+B_{15}^{(p)} H_0)}\right] \quad . \quad . \quad . \quad (6)$$

This formula holds also for the carbonic acid thermometer up to the number of decimals given by CHAPPUIS. In XV we shall further discuss the deviation of the formula used by CHAPPUIS.

With a sufficient degree of approximation the formula for the determination of the temperature down to 0°.001 with a hydrogen thermometer of 1100 m.M. zero point pressure and a dead space $\frac{u}{V_0}<0.01$ may be written in the simpler form:

$$H_T\left[\frac{V_0(1+k_1 t+k_2 t^2)+\beta_1+u_1}{A_T(1+B_T^{(p)} H_T)}+\frac{u_2'}{1+0.00366\, t_2'}+\right.$$

$$\left.+\frac{u_2''}{1+0.00366\, t_2''}+\frac{u_3}{1+0.00366\, t_3}+\frac{u_4}{1+0.00366\, t_4}\right]=$$

$$=H_0\left[\frac{V_0+\beta_2+u_1+u_2'+u_2''+u_2'''}{A_{T_0}(1+B_{T_0}^{(p)} H_0)}+\frac{u}{1+0.00366\times 15}\right] \quad . \quad . \quad . \quad (7)$$

First an approximate value may be assumed for $B_T^{(p)}$. With the approximate value of the temperature found in this way a better value of $B_T^{(p)}$ may be determined, and the correction term for the expansion of glass calculated.

Thus we find A_T, from which the value of θ follows through

$$\frac{A_T-A_{T_0}}{0.0036618}=\theta.$$

XV. *Influence of the deviation from the law of* BOYLE—CHARLES *on the temperature, measured with the scale of the gas thermometer of constant volume according to the observations with this apparatus.*

§ 1. When the formulae are drawn for the calculation of the temperature on the scale of the gas thermometer of constant volume the variation of pressure of the gas both in the thermometer-reservoir

and in the dead space has as yet (see e.g. CHAPPUIS) been generally entered into the calculation as if it took place at perfectly constant density.

The error committed in this way, is so slight for the permanent gases for small values of the dead space, that it manifests itself only in the last of the decimals given by CHAPPUIS. For CHAPPUIS' carbonic acid thermometer, however, it attains an appreciable value (the influence extends here to the last decimal but one), so that it was of importance to examine in how far it is permissible to neglect it. This appears when CHAPPUIS' formula is more closely compared with formula (6) of XIV.

The density not being constant, either in the thermometer-reservoir nor in the dead space, on account of the fact that e.g. at low temperatures gas passes from the dead space to the reservoir, and pv as well as the pressure-coefficient varies with the density, four approximations are applied in this treatment (two for reservoir and two for dead space), all giving an error in the same direction. (Adsorption is left out of account).

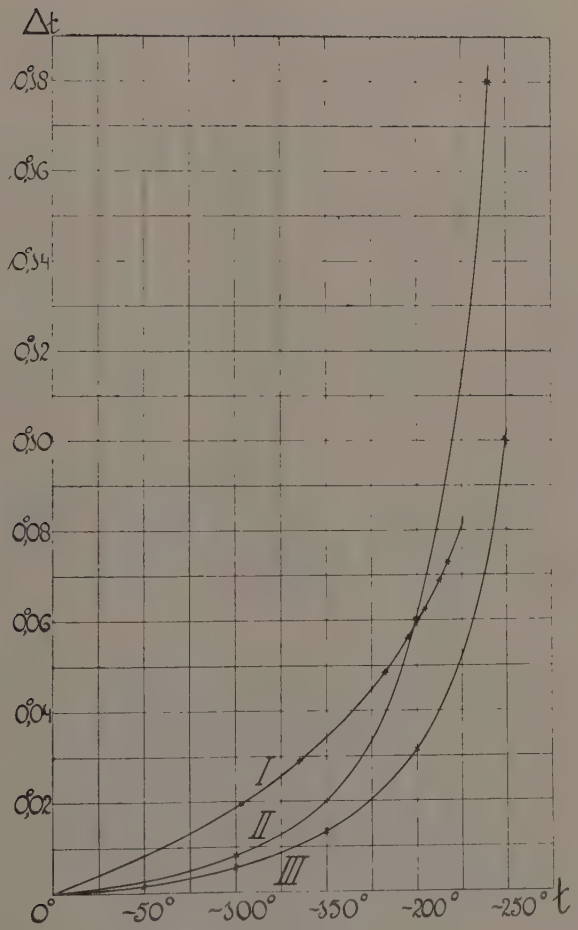
The errors caused by these approximations, are of the same order of magnitude for the reservoir and the dead space, the first applying to a large volume and a small difference of density, the second to a small volume and a large difference of density. The correction which is to be applied to the determination of temperature on account of these errors, only amounts to $-0°.001$ at $-100°$ for a hydrogen-thermometer with 1000 mm. zero-point-pressure and a dead space of $0.01\,V_0$, to somewhat less for lower temperatures, and so it may be neglected below 0°.

Formula (6) differs from the preceding formula by one correction more, which is independent of the size of the dead space, and which is the result of the variation of density in the reservoir caused by the expansion of the glass. This error is of no importance for the determination of the temperature by the hydrogen-thermometer, but may exercise an appreciable influence in some cases. (cf. § 3).

The approximations mentioned have also an influence on the determination of the mean pressure-coefficient. The discussion, perfectly analogous to that for the influence on the determination of the temperature, gives $+0.00000019$ as correction for our thermometer, which remains below the limit of accuracy given in Comm. N°. 60. Hence the value 0.0036627 derived in Comm. N°. 60 for hydrogen at 1090 mm. changes into the corrected value 0.0036629.

§ 2. We may pass from the temperatures derived in the way

Prof. H. KAMERLINGH ONNES and C. BRAAK. On the measurement of very low temperatures. XIV. Reduction of the readings of the hydrogen thermometer of constant volume to the absolute scale.



mentioned in Comm. N°. 95^e to those on the normal hydrogen-thermometer by availing ourselves of the subjoined table, in which the corrections required for this have been given. These corrections give an account of the variation in the assumed pressure-coefficient and (with regard to the number of decimals given) of the influence of the dead space.

TABLE XVIII. Corrections for the temperatures calculated according to Comm. N°. 95^e to those on the normal hydrogen scale.

t	Δt	t	Δt
— 50°	+ 0°.003	— 200°	+ 0°.016
— 100°	+ 0°.006	— 220°	+ 0°.019
— 150°	+ 0°.010	— 250°	+ 0°.020

By means of the fifth column of table XVI the corrections to the absolute scale are found. Thus the tables XVI and XVIII enable us to reduce the temperatures calculated according to Comm. N°. 95^e and used in Comm. N°s 95^a, 95^c and 95^d both to the normal hydrogen scale and to the absolute scale.

The temperatures t_s occurring in Comm. N°. 97^a, already corrected in the first column of table XVI for the application of the corrected pressure-coefficient 0.0036629 and the influence of the dead space, are adjusted to the absolute scale by the corrections in the fourth column of table XVI.

§ 3. The values found by CHAPPUIS and TRAVERS for the pressure-coefficient of hydrogen (cf. the footnote to § 7 of Comm. N°. 95^e) are corrected to 0.00366266 and 0.00366297 (number of decimals the same as given by them).

For the pression-coefficient of carbonic acid found by CHAPPUIS the correction is more considerable and amounts (because the dead space is small here, the correction on account of the variation of density caused by expansion of the glass is here about of the same value as that on account of the variation of density by the dead space) to -0.25×10^{-6}, so that the value found by CHAPPUIS [1]) 0.00372624 is corrected to 0.00372599.

[1]) Nouvelles Etudes, Travaux et Mémoires du Bureau International. T. XIII, p. 48.

Physics. — *"Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XV. *The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases."* By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Supplement N°. 15 to the communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of Februari 23, 1907).

§ 1. *Introduction.* In the Proceedings of Dec. '06, p. 502. (Comm. N°. 96*b*) it was mentioned that the investigation of the ψ-surface of binary mixtures in which the molecules of one component have extension but do not exert any attraction, would be taken in hand as a simpler case for a comparison with what the observations yield concerning mixtures of He, whose molecules are almost without cohesion. Before long we hope to give a fuller discussion of such a ψ-surface [1]). In the meantime some results have already been obtained in this investigation, which we shall give here.

Thus it has appeared, that at suitable temperatures, at least if the suppositions concerning the applicability of VAN DER WAALS' equation of state with a and b not depending on v and T for constant x, mentioned in § 2 hold for these mixtures, [2]) *two different phases may be in equilibrium which must be both considered as gasphases.* Then the two substances which are the components of these mixtures, are not *miscible in all proportions even in the gas state.* And if certain conditions are fulfilled this may continue to be the case when the one component is not perfectly without cohesion, but possesses still some degree of cohesion, which, however, must be very slight.

From the considerations of VAN DER WAALS, Contin. II p. 41 et sqq. and p. 104, follows that the mixing of two substances in the fluid state is brought about in consequence of the molecular motion depending on the temperature T, and promoted by the mutual attraction of the molecules of the two components determined by the quantity a_{12}, whereas the attractions of the molecules of each component inter se determined by a_{11} and a_{22}, oppose the mixing.

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[1]) VAN LAAR, These Proc. May '05, p. 38, cf. p. 39 footnote 1, treated the projection of the plaitpoint curve on the v, x-plane for such a mixture, without, however, further investigating the shape of the spinodal curve and of the plait.

[2]) The possibility of the occurrence of a longitudinal plait at temperatures above the critical ones of both components was supposed by VAN DER WAALS in his treatment of the influence of the longitudinal plait on critical phenomena. (Zittingsversl. Kon. Akad. v. Wetensch. Amst. Nov. 1894, p. 133). [Added in the English translation].

If the mutual attraction of the molecules of the two components a_{12} is small compared with the attraction of the molecules of one of the components inter se, a_{11}, the appearance of complete miscibility will be determined solely by the molecular motion, and then the temperature will have to be raised to an amount which, if some proportions of the b's can occur then, may greatly exceed the critical temperature of the least volatile component, T_{k_1} [1]), and with it the critical temperatures of all mixtures of these components. Thus from the equation (a) of VAN DER WAALS, Contin. II p. 43, follows $T_{km} = 1.6875\ T_{k_1}$ for the critical temperature of complete miscibility (VAN DER WAALS l. c.) T_{km}, if $a_{22} = a_{12} = 0$ and $b_{11} = b_{22}$ may be put. At a lower temperature the two substances considered are only partially miscible, whereas for such a temperature above T_{k_1} there may be coexistence of two phases which, as will be further explained in § 3 and 4, are to be considered as gas phases.

Now it seems to follow from the nature of most of the substances known to us, most likely from the structure of their atoms, that b_{22} is also small, when a_{22} becomes very small; hence for a gas without cohesion b_{22} may not be put equal to b_{11} of a gas with cohesion, and as according to the equation cited of VAN DER WAALS a small value of b_{22} furthers the mixing greatly, the critical temperature of complete miscibility cannot rise as high as was derived just now. But though most likely the case mentioned just now as example does not occur in nature, yet it is certainly conducive to a better insight of what is to be expected for gases of exceedingly slight cohesion.

§ 2. *The shape of the spinodal curves and the form of the plait on the ψ-surface for binary mixtures of which one component is a gas with molecules with extension and without cohesion.* In fig. 1 Pl. I the spinodal curves are represented for such a case. The figure refers to the ψ-surface for the unity of weight of the mixtures, as we hope to give a further discussion of such a ψ-surface (comp. § 1), also with a view to the treatment of the barotropic phenomena which may occur for these mixtures [2]) in case of a suitable proportion of the molecular volumes of the components, for which treatment the use of the ψ-surface for the unity of weight readily suggests itself. As was also mentioned in Comm. N°. 96 *b*, the conditions for

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[1]) VAN DER WAALS, in the paper cited p. 786 footnote [1], brought this in connection with the great amount of heat absorbed at the mixing of such substances. [Added in the English translation].

[2]) Cf. Comm. N°. 96 *a* (Nov. '06), 96 *b* (Dec. '06) and 96 *c* (Dec. '06, Febr. '07).

coexistence may be studied by the aid of the ψ-surface for the unity of weight in the same way as by the aid of that for the molecular quantity; moreover it is easy to pass from the former to the latter, which offers advantages for the treatment of many problems (cf. § 6) if this is desired.

The equation of the spinodal curve on the ψ-surface for the unity of weight of mixtures, for which VAN DER WAALS' equation of state for binary mixtures with a and b not depending on v and T for constant x may be applied, and for which $a_{12}=\sqrt{a_{11}a_{22}}$, $b_{12M}={}^1/_2(b_{11M}+b_{22M})$ (cf. Comm. No. 96*c*, Dec. '06, p. 510) may be put, [1]) runs:

$$R_1 R_2 Tv^3 = 2R_2(1-x)\{v\sqrt{a_{11}} - b_{11}\sqrt{a}\}^2 + 2R_1 x\{v\sqrt{a_{22}} - b_{22}\sqrt{a}\}^2.$$

Here R_1 and R_2 are the gas constants for the unity of weight of the components concerned. For $a_{22}=0$ this equation passes into:

$$4\tau\omega^3 = (1-x)[\{3\omega - (1-x)\}^2 + \frac{R_1}{R_2}\cdot\frac{b^2_{22}}{b^2_{11}}x(1-x)]$$

if we put $\frac{T}{T_{k_1}}=\tau$, $\frac{v}{v_{k_1}}=\omega$. The roots of this equation in ω have been determined by a graphical way for definite values of x and τ. The figure has been construed for mixtures for which $R_2/R_1={}^1/_2$, $b_{22}/b_{11}={}^1/_4$ (cf. Comm. N°. 96*c*, Febr. '07, p. 600, footnote 2).

With reference to Fig. 1 we point out that for $T<T_{km}$ ($=1.299\,T_{k_1}$) and $>T_{k_1}$ a spinodal curve closed on the side of the increasing v's, and together with it a similar plait, extends on the ψ-surface from the side of the small v's. At $T=T_{k_1}$ this plait reaches the side of the least volatile component. At lower T the spinodal curve has two distinct branches, and the plait runs in a slanting direction from the line $v=b$ to the side of the least volatile component.

Thus the investigation of mixtures with a gas without cohesion calls attention to a plait that starts from the side of the small volumes, and at lower temperature runs in an oblique direction to the side of the figure, which plait can be distinguished from the transverse and from the longitudinal plait.

The spinodal curve for $\tau=1.040$ has a barotropic plaitpoint P_b. (see Fig. 1). For $1.299<\tau<1.040$ the angle with the v-axis of the tangent to the plait in the plaitpoint [2]) $\theta_{pl}>\frac{\pi}{2}$, for $1.040<\tau<1$ is $\theta_{pl}<\frac{\pi}{2}$. The barotropic phenomena for such a plait will be further

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[1]) The quantities a_{11}, a_{22}, a_{12}, b_{11}, b_{22}, b_{12}, etc. relate to the unity of weight, $a_{11}{}^M$, a_{22M} etc. to the molecular quantity.

[2]) Cf. Comm. N°. 96*b*.

discussed in a following communication (cf. N°. 96c Febr. '07, p. 660, footnote 1).

In Fig. 2 the course of the plait has been schematically represented for a temperature between the barotropic plaitpoint temperature and the critical temperature of the first component. The — · — · — curves denote the pressure curves, the — — — — curve the spinodal curve, the continuous curve the connode. The straight line AB is the tangent chord joining the coexisting phases A and B, CD is the barotropic tangent chord (Comm. 96*b*).

§ 3. *Limited miscibility of two gases.* For mixtures where as in fig. 2 a plait giving rise to phases *separated by a meniscus* which coexist in pairs, represented in the figure e.g. by A and B, while mixtures in intermediate concentrations are not stable, extends on the ψ-surface from the side of the small v's at temperatures above the critical temperature of the least volatile component, we shall call not only the phase B a gas phase, for which it is a matter of course, but also the other A; so the latter may be called a *second gas phase*, and we may speak of *equilibria between two gaseous mixtures* at those temperatures. That there is every reason to do so in the case treated in § 2 appears already from this, that the reduced temperature of the phase A, calculated with the critical temperature of the unsplit mixture with the concentration of A, is so high that already through its whole character the phase must immediately make the impression of a gas phase (so a second one).

The shape of the p-lines in fig. 2 shows further, how the two coexisting gas phases may be obtained by isopiestic and isothermic mixing, in which nothing would indicate a transition to the liquid state, from the gas phases M and N of the simple substances [1]).

We shall explain in the following § that it is really in accordance with the distinction between gas state and liquid state for binary mixtures in general, when we call A a second gas phase.

§ 4. *Distinction between gas and liquid state for binary mixtures.* It is true that since the continuity of the gas and the liquid state of aggregation has been ascertained, it may be said with a certain degree of justice that it is no longer possible to draw the line between the two states, but when in the definition of what is to be understood by liquid and what by gas we wish properly to express the difference and the continuity in the character of the heterogeneous region and the homogeneous region and to preclude con-

1) Cf. footnote 1 p. 792.

clusions[1]) which are irreconcilable with the most obvious conception of phenomena, then the limits allowed for making this definition, are very narrow.

Thus for a simple substance no other distinction will be possible than by means of the isotherm of the critical temperature, and the border curve (connodal curve on GIBBS' surface), which is divided into two branches by the critical state (plaitpoint of the connodal curve), of which the branch with the larger volumes is to be defined as gas branch, that with the smaller volumes as liquid branch[2]). Liquid phases are only those which by isothermic expansion may pass into such as lie on the liquid branch of the connodal curve, and also the metastable[3]) phases lying between the connodal and the spinodal curves, which may be brought on the liquid branch of the connodal curve by isothermic compression[4]).

For binary mixtures the consideration of the ψ-surface of VAN DER WAALS leads in many cases to definitions which are just as binding.

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[1]) So THIESEN's definition, Z.S. für compr. und fl. Gase 1 (1897) p. 86, according to which e.g. strongly compressed hydrogen at ordinary temperatures would have to be called a liquid.

[2]) This is in harmony with the principle of *continuity of phase along the border curve* according to which a change of the character of the phases on a border curve can only occur in a critical point. For substances which at temperatures near the critical one, in states represented by points on or in the vicinity of that branch of the connodal curve on GIBBS's surface which connects the liquid states at low temperatures with the plaitpoint, should be associated to multiple molecules of which the volume is *greater* than the volumes of the composing molecules together, this principle would admit the possibility that on the liquid branch of the border curve liquid phases should occur with greater volume than the coexisting gasphase. Such simple substances would then show the barotropic phenomenon, till now only found for binary mixtures. There is nothing known that points in the direction, of making the existence of such simple substances probable but there can be no more given a reason why it should be impossible. [Added in the translation].

[3]) The metastable states have not been included in BOLTZMANN's definition Gastheorie II, p. 45.

[4]) We do not accept the principle of the distinction of LEHMAN, Ann. d. Phys. 22 (1907) p. 474: "Erst die unterhalb der betrachteten Isotherme liegenden Kurven, welche in ihrem *S*-förmigen Teil unter die Abszissenachse hinunterreichen, entsprechen wahrer (tropfbarer) Flüssigkeit, d. h. einem Zustand, der negativen Druck zu ertragen im stande is", as depending on the meaning that the existence of capillary surface tension in liquids which can form drops, would presuppose that these liquids can bear external tensile forces, i. e. negative pressures without splitting up (cf. ibid p. 472 in the middle, and p. 475 at the top). [Added in the translation].

When discussing this we shall leave out of account the case of solid states of aggregation and three phase equilibria.

In the first place gas states are all the states on the ψ-surfaces on which there are no plaits. As criterion to divide states which belong to the stable or metastable [1]) region of ψ-surfaces which show plaits, into gas states and liquid states, analogy with the simple substance indicates their relation with the connodal curves of those plaits while for the metastable states the help of spinodal curves is to be called in.

For this first of all the distinction between the two branches of the connodal curve of a plait is required. For in the first place we shall have to give the same name to each of the two branches of a connodal curve separated by one or two plaitpoints throughout its length [2]).

Now, on account of the existence of the barotropic phenomenon we cannot simply call gas branch of the connodal curve that at which one of the isopiestically connected states has the smallest density [3]). It is therefore the question to indicate if possible on each branch a state whose nature is already known through the definition holding for simple substances or for those which behave as such when splitting up into two phases. In this different cases are to be distinguished.

For the case that the considered plait [4]) extends from one of the side planes $x = 0$ or $x = 1$ over the ψ-surface, follows from the definition of gas phase and liquid phase of a single substance that the branch of the connodal curve from the gas state of the pure substance to the plaitpoint is to be called gas branch, and also that the branch from the liquid phase of the simple substance to the plaitpoint is to be called liquid branch. The gas branch and the liquid branch of the spinodal curve may be distinguished in the same way as those of the connodal curve.

Let us restrict ourselves for the present to the distinction of gas and liquid in this case. In the first place we make use for this purpose of the isomignic (Comm. N°. 96*b*) compression and expansion.

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[1]) It follows from the nature of the case that unstable states have not to be considered here.

[2]) Cf. p. 790 footnote [2].

[3]) Even it if we wish to leave gravity out of account, and pay only attention to the molecular volume of the phase, the barotropic phenomena have yet called attention to the possibility that we may find the gas volume first larger and then smaller than the liquid volume when passing along the same connodal curve.

[4]) The case of the two plaits at minimum critical temperature is comprised in this.

Every phase which cannot be brought on the connodal curve through this operation, or if it can, comes on the gas branch, will have to be called a gas phase, every phase which is made to lie on the liquid branch through isomignic expansion is a liquid phase. Besides the phases lying between the connodal and the spinodal curve which isomignically may be brought on the liquid branch of the connodal are metastable liquid phases.

Besides the isothermic and isomignic compression without splitting there is another operation already mentioned in § 3, which may help us to form an opinion about the similarity of different phases, viz. the isopiestic and isothermic mixing. [1]) With regard to this phases which have been obtained by isopiestic admixing without splitting from phases of which it has been ascertained that they are to be called liquid phases, must be called liquid phases until in another way, (e. g. because no splitting takes place with isomignic compression and expansion) they have been proved to have passed into gas phases. [2]).

Proceeding to the case that the plait from higher temperature appears as a closed plait on the ψ-surface, as long as the plaitpoint which first comes into contact with the side with decrease of temperature, has not yet come into contact, and with decrease of temperature the plait has not yet reached a mixture which on splitting behaves as a simple substance, and for which the distinction in liquid state and gas state is therefore fixed, we shall have to consider that branch of the connodal curve on the side of this plaitpoint, which passes into that of the gas phase at lower temperature, as belonging to the ordinary gas phase, whereas the branch which passes into the liquid branch at lower temperature may be looked upon as a *second gas phase*, and we are the more justified in doing so as the temperature should lie further above the critical tempera-

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[1]) With the continuous isothermic and isopiestic mixing of two similar phases a and b the case may present itself (divided plait in the case of minimum crit. temp.), that an intermediate phase c of the other kind is obtained. So in general we cannot conclude to the similarity of c from the isothermic and isopiestic mixing of similar a and b.

[2]) This criterion is particularly of application to the retrograde condensation 2nd kind. For then phases on the connodal curve between the plaitpoint and the critical point of contact are liquid phases, phases on the p-curve through the plaitpoint and phases with the same x as the critical point of contact just the transitions to gas phases. The phases within the triangle bounded by these two lines and the connodal curve are also to be considered as liquid phases.

Here we abstract from the small uncertainties which would be caused in these definitions when capillarity ought to be taken into account. [Added in the translation].

tures of the unsplit mixtures belonging to the phases lying on them.

Whereas in the case, that at a temperature comparatively little lower also the other side of the ψ-surface is reached by the originally closed plait, the difference of the second gas phase with a liquid phase is still not very conspicuous, this may become very clear for the case of § 2, to which we have now got at last, that viz. with decreasing temperature a plait comes from the side $v = b_x$ on the ψ-surface, and the plait appears for the first time as longitudinal plait. Now we may again call *PBDF* the branch of the first gas phase, *PACE* the branch of the second gas phase. It will certainly be obvious to speak of gas phases when *all* the parts of the plait are found above the critical temperatures of the unsplit mixtures, and we shall decidedly *have* to speak of two gas phases, when the second branch of the connodal curve is intersected all over its length by isomignic lines on which beyond this plait no splitting up occurs, or if it is at most touched by one of them in the point $v = b$. For then it is beyond doubt that the final point of that branch must be called a gas phase.

Possibly also phases between the isomignic line of the critical point of contact, the line $v = b_x$ and the second gas branch belong to the second gas phase.

§ 5. *The surface of saturation for equilibria on the gas-gasplait.* In fig. 3, 4 and 5 the sections $T =$ const. of the p, T, x-surface of saturation for equilibria on the gas-gasplait have been schematically drawn for a mixture in which one component is a gas without, or almost without cohesion, in fig. 3 and 4 for temperatures higher than the critical temperature of the first component, in fig. 5 for this last temperature.

In these figures too the division of a gas phase into two gas phases, and the transition of a part of the gas region into the liquid region at $T = T_{k_1}$ is clearly set forth. The — — — — curve is the locus of the plaitpoints.

In a following communication, in which the properties of the ψ-surface for such mixtures will be further discussed, T, x-sections etc. will be drawn of this surface of saturation. At the same time it will then have to appear in how far *retrograde* unmixing of a phase into two other phases is to be expected.

That one of these phases may be called a second gas phase, appears in § 4.

§ 6. *On the conditions which must be fulfilled that limited mis-*

cibility of two gases may be expected. Now that it has appeared that on the suppositions mentioned in § 2 for mixtures in which one component is a gas without cohesion with molecules with extension, limited miscibility might be expected in the gas state, the question rises whether this phenomenon is also to be expected for mixtures with a gas of feeble cohesion. As on the said suppositions no maximum critical temp. is to be expected, this will be the case when $T_{km} > T_{k_1}$ is found. [1]) We have treated this question by the aid of the ψ-surface for the molecular quantity (cf. § 2). We arrive then at the equations developed by VAN DER WAALS Contin. II p. 43. The condition that $T_{km} > T_{k_1}$ is:

$$\{b_{22M}/b_{11M} - \sqrt{a_{22M}/a_{11M}}\}^3 > \frac{4}{27} b^3{}_M/b^3{}_{11M} \cdot \frac{1}{x_M(1-x_M)}$$

in which b_M and $x_M(1-x_M)$ follow from the equations given by VAN DER WAALS loc. cit. We find from this [2]) $T_{km} > T_{k_1}$,

for	$b_{22M}/b_{11M} = 2$	, if $a_{22M}/a_{11M} < 0.58$
	1	0.053
	$^1/_2$	0.0037
	$^1/_4$	0.00023
	$^1/_8$	0.000015

It appears on investigation that only for few pairs of substances the ratios of the a's and b's [3]) will be able to satisfy this condition. The still unknown relations between a and b for a same substance, to which we alluded in § 1, and from which ensues that in general substances with small a also possess a small b, and that as a rule large b goes together with large a, seem to prevent this. He, which with a b which is still not very small compared with H_2 possesses a very small a, so feeble cohesion, and H_2O, which taking the value of a into consideration, has a comparatively small b, so a molecule of small volume, constitute exceptions to this general rule which are favourable for the phenomenon treated here.

If for $He - H_2$: $b_{22M}/b_{11M} = ^1/_2$, and $a_{22M}/a_{11M} = ^1/_{175}$ (Comm. N°. 96c, Febr. '07. p. 660 footnote 2), $T_{km} < T_{k_1}$ must be expected on the above suppositions. Also for helium-argon and helium-oxygen e. g. the same thing must be expected. Most likely the ratios are

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[1]) Whether limited miscibility in the gas state may also occur if $T_{km} < T_{k_1}$ in certain cases and at suitable temperatures, will be discussed in § 7.

[2]) For $b_{22M}/b_{11M} = ^1/_8$ e g. we find also $T_{km} > T_{k_1}$ for $0.125 > a_{22M}/a_{11M} > 0.061$. These cases will be further discussed.

[3]) See e. g KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen.

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Plate I.

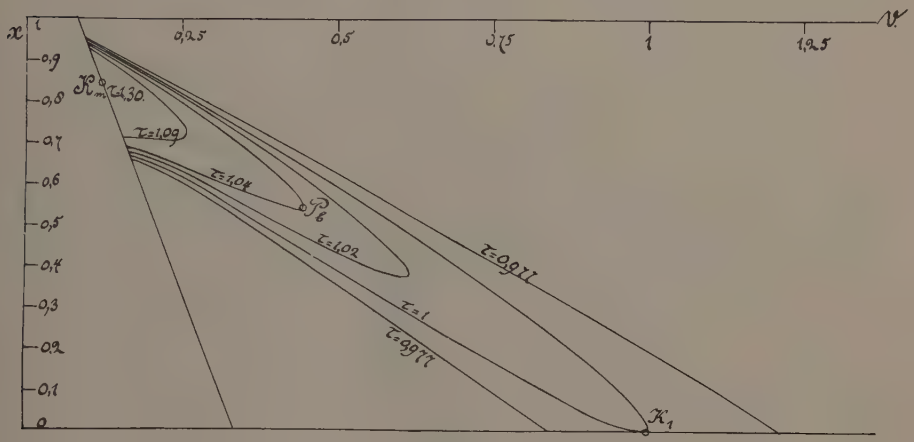

Fig. 1

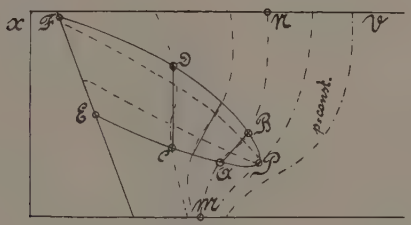

Fig. 2.

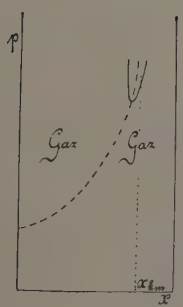

Fig. 3.

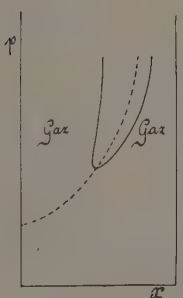

Fig. 4.

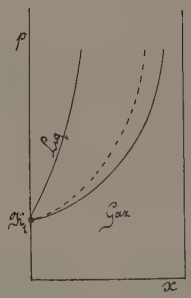

Fig 5

more favourable for mixtures of helium and neon [1]) than for those of helium and hydrogen.

For mixtures of helium and water the ratios for the above assumed a_{He} and b_{He} are such that for them limited miscibility in the gas state is to be expected, if the suppositions mentioned in § 2 are to be applied.

The coefficients of viscosity and of conduction of heat (cf. Comm. N°. 96*c*, Febr. '07 p. 660 footnote 2) admit a value of b_{He} which is still somewhat though only little higher; this might render it possible to realise the said phenomenon perhaps also for the other pairs of substances mentioned, especially when we bear in mind that its appearance is not excluded for $T_{km} < T_{k_1}$ (cf. p. 794 footnote 1).

The experimental investigation of these mixtures has been taken in hand in the Leiden Laboratory.

(Communicated in the meeting of March 30).

§ 7. *The shape of the spinodal curves and of the plaits for the case that the molecules of one component exert some, though still feeble attraction.* With very small value of the mutual attraction a_{12} of the molecules of the two components, in connection with the feeble attraction a_{22} of the molecules of one component inter se, the spinodal curve will with decreasing temperature extend more and more on the ψ-surface as in Pl. I fig. 1 from the side of the small v's, come into contact with the line $x = 0$ at $T = T_{k_1}$, and then cross from the line $v = b$ to the side $x = 0$ in two isolated branches [2]). We leave here out of account what takes place at lower temperatures when the spinodal curve approaches and reaches the side $x = 1$ too.

To examine what shape the spinodal curve can have with greater attraction of the most volatile component, we shall avail ourselves of the suppositions introduced in § 2 and also applied in § 6 con-

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[1]) Cf. RAMSAY and TRAVERS, Phil. Trans. A. 197 (1901) p. 47 for data concerning refractive power and critical temperature of neon.

[2]) Here $\frac{dT_{xpl}}{dx} > 0$ for $x = 0$. We see here that VERSCHAFFELT's conclusion (These Proc. March 1906 p. 751) concerning the maximum temperature in the plaitpoint curve for mixtures, for which the component is indicated by a point from the region *OHK* (see fig. 2) must be supplemented by the possibility that he branch of the plaitpoint curve starting from the first component, goes to infinite pressures.

cerning the equation of state and the quantities a_{12} [1]) and b_{12}. In the net of spinodal curves for a given pair of substances 2 singular points may then occur, belonging to the spinodal curves for different temperatures. The values of x for these are determined by the equation:

$$\frac{x_M}{1-x_M} = \frac{3b_{11M}\sqrt{a_{22M}} \mp 2b_{11M}\sqrt[4]{a_{11M}a_{22M}} - b_{22M}\sqrt{a_{11M}}}{-b_{11M}\sqrt{a_{22M}} \mp 2b_{22M}\sqrt[4]{a_{11M}a_{22M}} + 3b_{22M}\sqrt{a_{11M}}} \quad (1)$$

For very small a_{22} we find from this two singular points with $x > 1$, so not belonging to that part of the ψ-surface which can denote phases of mixtures. Of these two singular points that for which the lowest signs hold, passes through infinity for increasing a_{22}, and then approaches the line $x = 0$ on the other side of the ψ-surface. This line is reached for:

$$\sqrt[4]{a_{22M}/a_{11M}} = \frac{1}{3}\{-1 + \sqrt{1 + 3\,b_{22M}/b_{11M}}\} = m_1 \quad . \quad (2)$$

With increasing a_{22}/a_{11} the singular point, which appears to be a double point for this region, approaches the line $v = b$, which line is reached for:

$$\sqrt[4]{a_{22M}/a_{11M}} = -(1-b_{22M}\,b_{11M}) + \sqrt{1-b_{22M}/b_{11M}+(b_{22M}/b_{11M})^2} = m_2 \quad (3)$$

In this we assume $b_{22M} < b_{11M}$ [2]).

So if the mutual attraction of the molecules of the most volatile component and those of the other in connection with the attractions inter se attains a certain value — on the assumptions made for the calculations for $m = \sqrt[4]{a_{22M}/a_{11M}} = m_1$ — the spinodal curve for $T = T_{k_1}$ will no longer touch the side in K_1 (cf. fig. 1 Pl. I), but it

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[1]) In this first investigation of what may be expected for mixtures of helium, with a view of forming some opinion as to the conditions under which the experiments for this purpose are to be made, we put (§ 2), $b_{12M} = \frac{1}{2}(b_{11M} + b_{22M})$ $a_{12M} = \sqrt{a_{11M}a_{22M}}$ (cf. Comm. Suppl. No. 8, These Proc. Sept. '04 p. 227) in the calculations, no data concerning a_{12} and b_{12} for those mixtures being available as yet. Also VAN DER WAALS (These Proc. Febr. '07, p. 630) assumes that as a rule $a_{12M} < (a_{11M} + a_{22M})$. It will be necessary for a complete survey concerning the different possibilities to make also other suppositions about a_{12M} (cf. VAN DER WAALS l.c., KOHNSTAMM ibid p. 642), at the same time taking care that a and b are not put independent of v and T. at least not both (cf. VAN DER WAALS, These Proc. Sept. '05 p. 289) and that they may only be put quadratic functions of x by approximation.

If also for mixtures with very small a_{22}, a_{12M} might be $< \sqrt{a_{11M}a_{2M}}$ (cf. KOHNSTAMM l c.). the phenomena of limited miscibility under discussion might still be sooner expected.

[2]) For $b_{22M} > b_{11M}$ the other singular point comes from side $x = 1$ on the ψ-surface for a smaller value of a_{22M}/a_{11M}. As probably this case does not present itself for the pairs of substances with small a_{22}/a_{11} known to us, we shall not discuss it.

will have a double point there, in which the two branches of the spinodal curve intersect each other and the line $x = 0$ at an angle. In this case the critical temperature of the least volatile component is not changed in first approximation by small quantities of admixtures.

With greater attraction of the most volatile component — on the suppositions mentioned for $m_1 < m < m_2$ — a spinodal curve on the ψ-surface will have a double point. This will lie the nearer to the side of the small v's, the more the attraction of the most volatile component increases. With a certain value of the attraction — $m = m_2$ — the spinodal curve reaches the line $v = b$ with a double point, with greater attraction the spinodal curve will proceed from $x = 0$ on the ψ-surface with decreasing T, and touch the line $v = b$ at $T = T_{km}$. On the suppositions mentioned for $b_{22M}/b_{11M} < {}^{16}/_{21}$ the contact with the line $v = b$ will here take place at temperatures $> T_{k_2}$, for $b_{22M}/b_{11M} > {}^{16}/_{21}$ at $T < T_{k_2}$, so that in the latter case the spinodal curve comes first into contact with the line $x = 1$.

In the first case ($b_{22M}/b_{11M} < {}^{16}/_{21}$) a plait will come from $x = 0$ and at lower T, whereas for larger m a branch plait directed to the side $x = 1$ may develop: if $m < m_2$ it will be united through an homogeneous double plaitpoint (KORTEWEG, *Archiv. Neerl.* 24 (1891)), with a plait coming from $v = b$ to a plait that crosses from one side to the other, if $m > m_2$ it will pass into such a plait by contact with $v = b$.

In the second case the plait which becomes from $x = 0$ will again united with one coming from $v = b$ for smaller m; for larger m a branch plait will have developed before this union takes place or before the spinodal curve touches the line $v = b$.

The shape of the spinodal curve for these cases with always greater attraction of the most volatile component, where we shall have to consider three phase equilibria, need not be discussed for the present, as they do not belong to the case of a component with feeble attraction [1]).

For some values of b_{22M}/b_{11M} table I gives the values $a_{22M}/a_{11M} = m^4$, calculated from the equations (2) and (3). If we compare with this the values of a_{22M}/a_{11M} for which $T_{km} = T_{k1}$ (§ 6) we see that they really lie between those calculated here.

The shape of the spinodal curves for a case, in which $m_1 < m < m_2$, has been represented on plate II, for the ψ-surface of the unity of weight (cf. § 2), with the relations and data assumed in § 2, except that $a_{22}\, a_{11} = 0.00049$ (or $a_{22M}/a_{11M} = 0.00196$).

[1]) Cf. moreover VAN LAAR, Arch. TEYLER (2) 10 (1906), These Proc. Sept. '06 p. 226.

TABLE I.

b_{22M}/b_{11M}	m_1^4	m_2^4
$1/2$	0.0014	0.0179
$1/4$	0.000134	0.000527
$1/8$	0.000011	0.000022

The plait extending on the w-surface from $v = b$ for a temperature $> T_{k1}$, will have to be considered as a gas-gasplait according to § 4 (cf. § 6). Also a similar plait for $T < T_{k_1}$, if the connodal curve is not touched by an isomignic line, and is nowhere cut by an isomignic line which intersects the connodal curve of the plait coming from $x = 0$ [1]. According to § 4 we shall be justified in considering also the plait lying on the side of the small v's for $T_{k_1} > T > T_{dpl}$ (temperature for which the double plaitpoint considered occurs) as gas-gasplait, if the temperature is above the critical temperatures of the unsplit mixtures for all parts of that plait. That there can be some reason for doing so, appears when we calculate the reduced temperature for the double plaitpoint for some cases, e.g. for the ratios b_{22M}/b_{11M} and the m_2 belonging to it, mentioned in Table I.

Putting $b_{22M}/b_{11M} = n$ the double plaitpoint temperature is determined by :

$$T_{dpl}/T_{k_1} = \frac{27}{4}\, m\,(1+m)\,\frac{(n-m^2)^2}{(n+m)^3}$$

and

$$v_{dpl}\; v_{k_1} = \frac{2}{3}\,\frac{m}{(1+m)^2}\cdot\frac{(n+m)^2}{m\,(2-m)-n\,(1-2m)}$$

So for the case represented on Plate II we find :

$$x_{dpl} = 0.587,\quad T_{dpl}/T_{k_1} = 0.966,\quad T_{dpl}/T_{kx} = 2.17.$$

(*To be continued*).

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[1]) Here it appears that a gas-gasplait can occur also if $T_{km} < T_{k_1}$, and for temperatures $T < T_{k_1}$ with $T_{km} > T_{k_1}$, (cf. p. 794 note 1 and p. 794).

(April 25, 1907).

H. KAMERLINGH ONNES and W. H. KEESOM. Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases.
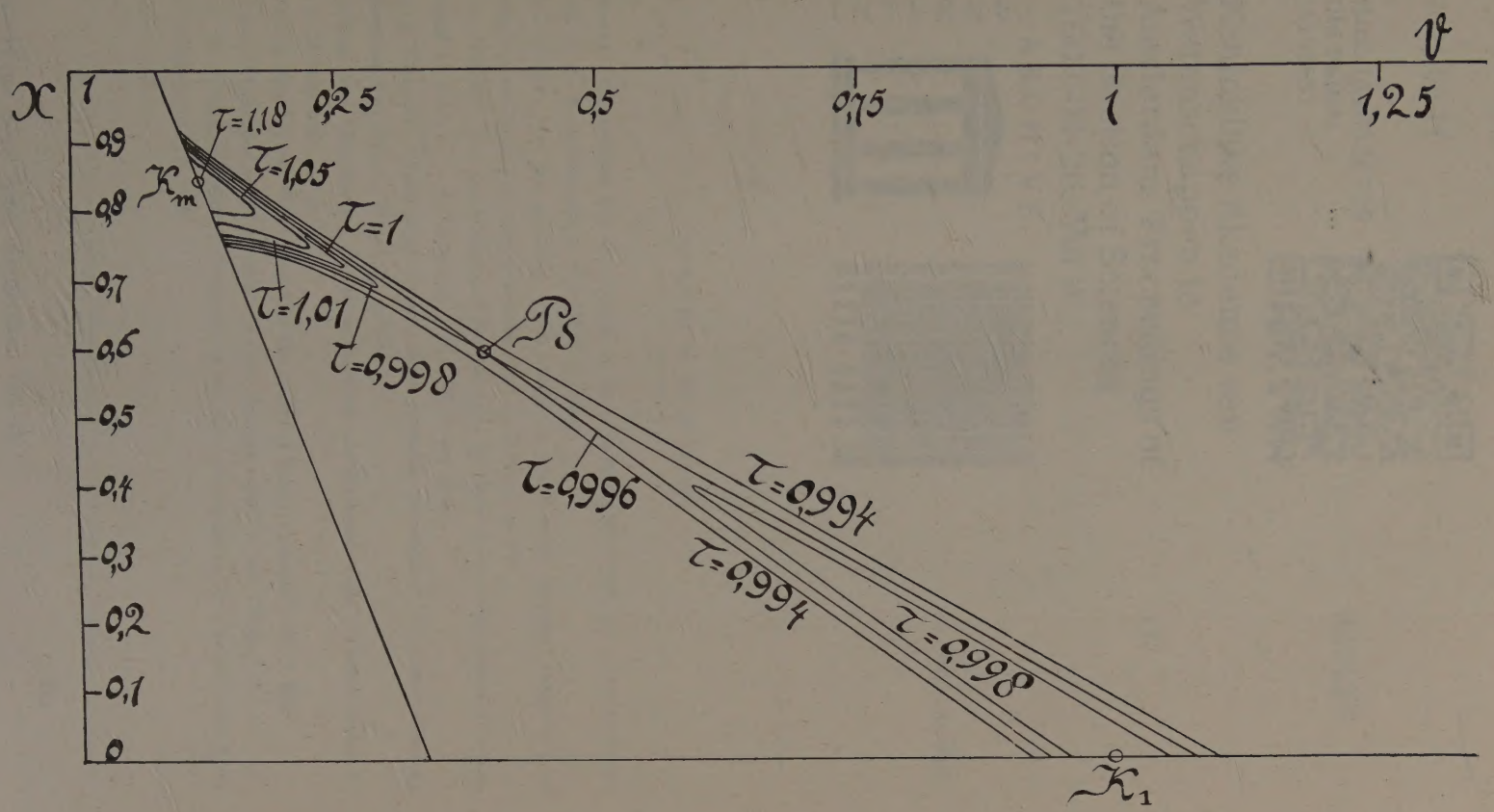
Plate II.